# THE 3 P's OF COATING: PRINTING, PACKAGING & POINT OF SALE

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March 27th & 28th 2007

ROBINSON COLLEGE
CAMBRIDGE

# PITA COATING CONFERENCE 2007

**Paper Industry Technical Association**
**5 Frecheville Court,**
**Bury, Lancashire**
**BL9 0UF**

## CONFERENCE PROCEEDINGS

PAPER INDUSTRY TECHNICAL ASSOCIATION

# 2007

# COATING CONFERENCE

## THE 3 P's OF COATING:
## PRINTING, PACKAGING & POINT OF SALE

*Organised by the*
*PITA Coating Working Group*

**CONFERENCE PROCEEDINGS**

*27th & 28th March 2007*

# COATING CONFERENC

## "THE 3 P'S OF COATING

**Tuesday 27th March**

## Tuesday, 27th March 2007

| | | | |
|---|---|---|---|
| 09.00 | | Welcome from Conference Chairman | Ian Davis,<br>*Chair, PITA Coating Working Group* |

**SETTING THE SCENE**

| | | | |
|---|---|---|---|
| | | Retail Ready Packaging – A European Perspective | Karen Bevan,<br>*IGD* |

### SESSION 1 ... "EQUIPMENT – THE APPLIANCE WITH SCIENCE!"

*Session Chairman* - **Andrew Griffiths,** *BTG UK Ltd*

| | | | |
|---|---|---|---|
| 09.45 | Paper 1 | Coating Machine Rebuilds - A Tool to Enhance Quality and Efficiency | Lauri Korhonen,<br>*Metso Paper* |
| 10.15 | Paper 2 | Blade Technology - A Tool for Improved Print Quality | Kenneth Fagrelius,<br>*BTG Duroblade SA* |
| 10.45 | | **Coffee** | |
| 11.15 | Paper 3 | Free Jet Coating - Recent Experiences with "Closed Head" Design | Paolo Rabito,<br>*PMT Italia* |
| 11.45 | Paper 4 | New Technology to Measure the Parallelism of Rollers | Matthias Ecker,<br>*Pruftechnik Ltd* |
| 12.15 | Paper 5 | The Fourth P; Power and How to Save it to Make Money | Tim Klemz,<br>*Compact Engineering Ltd* |
| 12.45 | | **PITA AGM** | |
| 13.00 | | **Lunch** | |

### SESSION 2 ... "TWO MORE P'S: PIGMENTS AND POLY-THINGS!"

*Session Chairman* - **Steve Mann,** *Paper Classroom*

| | | | |
|---|---|---|---|
| 14.15 | Paper 6 | Design of Coating Structure for Flexographic Printing | Janet Preston,<br>*Imerys Minerals* |
| 14.45 | Paper 7 | Use of a Steric Stabilizer as Water Retention Aids for Maximising Calcium Carbonate Use in Glossy Coated Paper | Francois Dupont, *Coatex SAS*<br>Mark Smith, *Omya UK* |
| 15.15 | Paper 8 | Titanium Dioxide and Zinc Sulphide: High Quality Pigments for Special Papers | Jorg Hocken,<br>*Sachtleben GmbH* |
| 15.45 | | **Tea** | |
| 16.15 | Paper 9 | Replacement of Latex by Natural Polymer Bindings in Coating | Frederic Bouvier,<br>*Roquette (UK) Ltd* |
| 16.45 | Paper 10 | Aqueous Dispersions of Polyolefins | Ronald Wevers,<br>*The Dow Chemical Company* |
| 17.15 | Paper 11 | Optimisation of the Coating Colour Kitchen in the New Environment of the Paper Mills | Thierry Leduc,<br>*ABB Cellier* |
| 17.45 | | End of Day One | |
| 19.30 for 20.00 | | **Conference Dinner** | |

# PROGRAMME

ROBINSON COLLEGE
CAMBRIDGE

# RINTING, PACKAGING & POINT OF SALE”

## Wednesday, 28th March 2007

### SESSION 3 ... “FORMULATIONS – MIXING IT WITH THE BEST”

*Session Chairman* - **Chris Hindley,** *Ciba Specialty Chemicals*

| | | | |
|---|---|---|---|
| 09.00 | Paper 12 | Cost Reduction through Optimisation of Coating Formulations | Mariela Gauto,<br>*Clariant* |
| 09.30 | Paper 13 | Effect of Water Retention and Rheology Modifier (WRRM) Chemistry on Paper Coating Structure | Tamal Ghosh,<br>*Ciba Specialty Chemicals* |
| 10.00 | Paper 14 | Material Retention: A Novel Approach to Performance of Pigment Coating Colours | Jaana Ahtikari,<br>*CP Kelco Oy* |
| 10.30 | Paper 15 | Today’s Trend Lines in Coating Kitchens, Supply Systems and Coating Effluent Treatment | Ilkka Roitto,<br>*Metso Paper* |
| 11.00 | | **Coffee** | |
| **ROUND TABLE** | | With a focus on Energy Usage in Coating<br>*Moderator* - **Ian Davis,** *IMD Consulting*<br>*Panel to be selected from speakers and other experts* | |
| 13.00 | | **Lunch** | |

### SESSION 4 ... “ASPECTS OF PACKAGING AND PRINT – FOR THE ULTIMATE CUSTOMER”

*Session Chairman* - **Kieran Rafferty,** *RaKeM Ltd*”

| | | | |
|---|---|---|---|
| 14.15 | Paper 16 | Design and Engineering of Mineral Fillers for Barrier Coatings | Dave Gittins,<br>*Imerys Minerals* |
| 14.45 | Paper 17 | New Development in Print Receptive and Barrier Coatings | Robin Cooper,<br>*Michelman Inc* |
| 15.15 | | **Tea** | |
| 15.45 | Paper 18 | Print, Packaging and Product Uniformity - Issues through the Production Cycle | Nigel Jopson,<br>*Pira International* |
| 16.15 | Paper 19 | Measuring and Evaluating the Surface Quality of Gravure Papers. | Dr Harald Grossman,<br>*Dresden University /PTS* |
| 16.45 | Paper 20 | A Re-evaluation of Factors Controlling Print Rub on Matt and Silk Coated Papers | Pat Gane,<br>*Omya Development AG* |
| 17.15 | | **Closing Remarks and End of Conference** | |

Wednesday 28th March

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## SESSION 1 ... "EQUIPMENT – THE APPLIANCE WITH SCIENCE!"

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## SESSION 3 ... "PRINTING, PACKAGING & POINT OF SALE"

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# index by session

**Conference Chairman: Ian Davis**
**Chairman, PITA Coating Working Group**

**Session Chairman: Andrew Griffiths**
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*Tuesday, 27th March 2007 09.00*

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**Ciba Specialty Chemicals**

*Wednesday, 28th March 2007 09.00*

**Session Chairman: Kieran Rafferty**
**RaKeM Ltd**

*Wednesday, 28th March 2007 14.15*

# Coating Machine Rebuilds - A Tool to Enhance Quality and Efficiency

*by*
**Lauri Korhonen & Kari Sorsa**
Metso Paper, Finland

SESSION ONE
PAPER ONE

## Introduction

The efficiency and profitability of a paper or board making line can be significantly improved, not only through major capital investments, but also by various limited scope rebuild and upgrade solutions. Minimized waste, improved overall efficiency, enhanced quality and increased speed potential are among the many benefits which can be obtained through a range of process improvements.

This paper presents practical mill experiences of undertaking such limited scale rebuild projects.

## Improved quality and productivity with coating head modifications

### *New blade beam on existing coating station*

By replacing the blade beam on an existing coating station, it is possible to improve coat weight profiles and their control. At the same time, it is possible to increase the blade angle operating range as well as improve runnability. Enhanced coater control capabilities improve paper quality, minimize waste, enable faster targeting of product quality following breaks and consequently ensure a positive boost to overall machine operating efficiency.

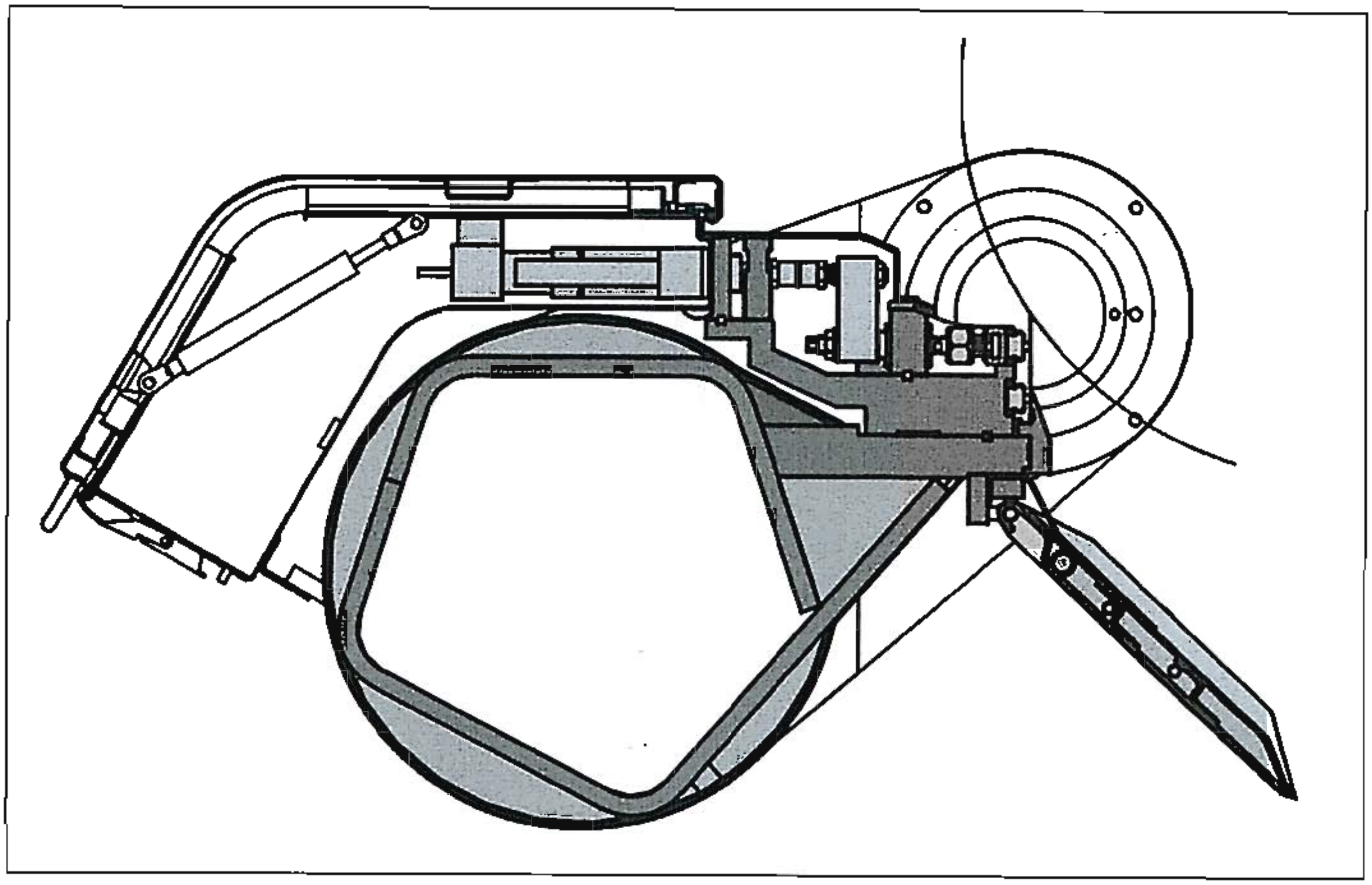

Figure 1. Blade beam with automatic profiling

*Automatic CD-profiling on existing blade coaters and sizers*

Cross-direction coat weight uniformity is an important factor in operating efficiency for both blade coaters and sizers - especially operation immediately following blade/rod changes or web breaks. High resolution actuators with an automatic coat weight profile control system offers the best tool for efficient CD profiling. The profilers are automatically adjusted to the optimal "start" setting following a web break or blade/rod change. The system allows rapid smoothing of the coat weight profile, which reduces the amount of broke produced following re - starts. Higher coat weight levels can also be achieved without sacrificing coatweight profile quality. Automatic CD-profiling improvements are applicable to off-line as well as to on-line coating machine lines.

*Production results*

The poor coat-weight profiles from an off-line coater were creating additional costs on a magazine paper production line. The quality problems became apparent only at the end of the production process, when the paper was ready for shipping. The mill had identified the blade beams on the coating heads as the main source of profile problems.

The existing coating heads were rebuilt with new blade beams having automatic straightness control and coat weight CD-profile control. Since the rebuild, the mill has been able to significantly reduce the percentage of customer rolls rejected during quality control. At the same time the overall operational efficiency has improved by 2 percentage points.

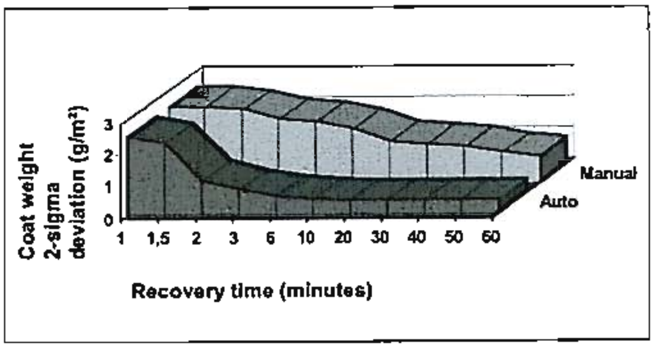

Figure 2. Coat weight deviation

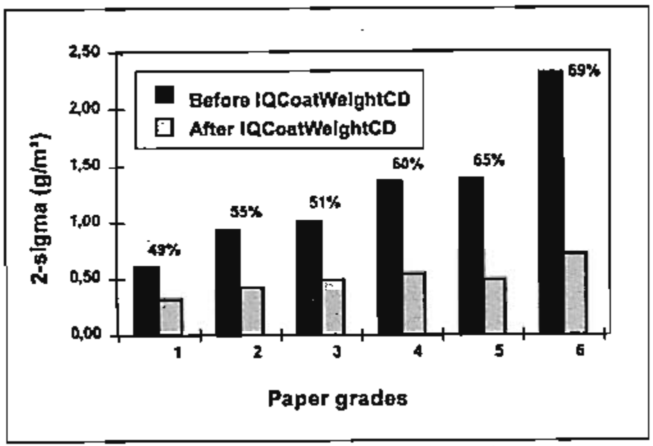

Figure 3. Automatic CD- profiling, 2 -sigma improvements

## Improved safety and reduction in waste with automatic backing roll cleaning device

The automatic backing roll cleaning device reduces broke by minimizing waste related to the washing of coating heads. It offers a faster, more efficient and more reliable cleaning compared to conventional manual washing methods. The roll cleaning device keeps the backing roll constantly clean (automated cleaning), which leads to a significant reduction in washing waste. The optimisation of wash water usage which it allows eliminates cleaning-related web breaks. Its automated operation also significantly improves operator safety.

The automatic backing roll cleaner cleans the backing roll quickly and automatically by wiping it with a cross-machine traveling sponge and water. It can be used during both normal production and during web breaks. It cleans the backing roll automatically after a flying splice on off-machine coaters, and during reel turn-up, or periodically, in on-machine coaters. On both machine types cleaning can be manually controlled from the local control box. This enables cleaning of the backing roll, zone-by-zone.

*Production results*

A wood free coated paper production line was suffering from excess bottom waste, which had a direct influence on productivity. The automatic roll cleaning device was installed on the jet coating stations of the off-machine coater in order to minimize the bottom waste and increase production.

The system installed at the mill cleans the backing roll quickly and automatically following a flying splice by wiping with a sponge and water. This solves the problem of excessive waste at the reel spool which was previously caused by random wet washing of the backing roll, or else by leaving the roll uncleaned. Reduced waste at the beginning of a new parent roll means more saleable paper. This was the key target for the mill, which now has been achieved.

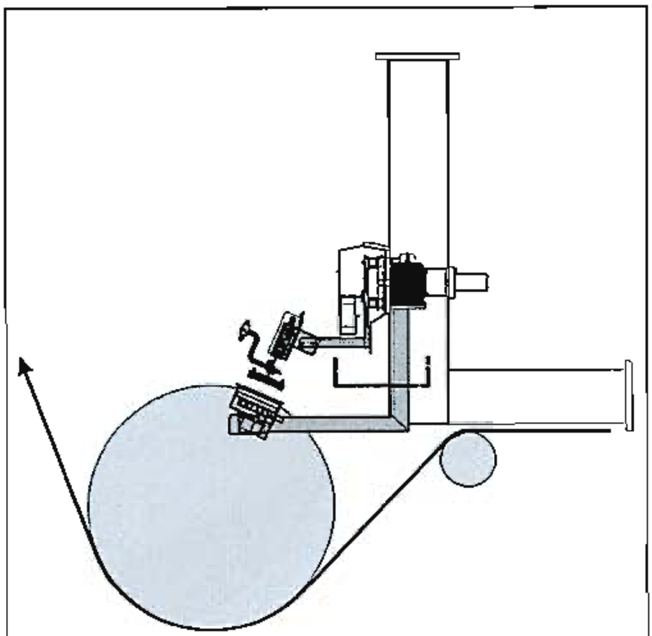

Figure 4. Automatic backing roll cleaner

After successful installation and start-up of the new cleaning system, the mill has been able to reduce excess bottom waste losses by 80 %. Operator safety has also improved. Manual roll cleaning inevitably involves certain risks. Following installation of the automatic roll cleaning device, the mill has eliminated the occurrence of strain injuries related to roll washing.

## Improved time efficiency with advanced tail threading

The tail threading system in the surface treatment section has a great impact on the time efficiency of the paper making line overall. Successful tail threading can only be ensured by the right tail threading equipment, used in conjunction with a well designed layout.

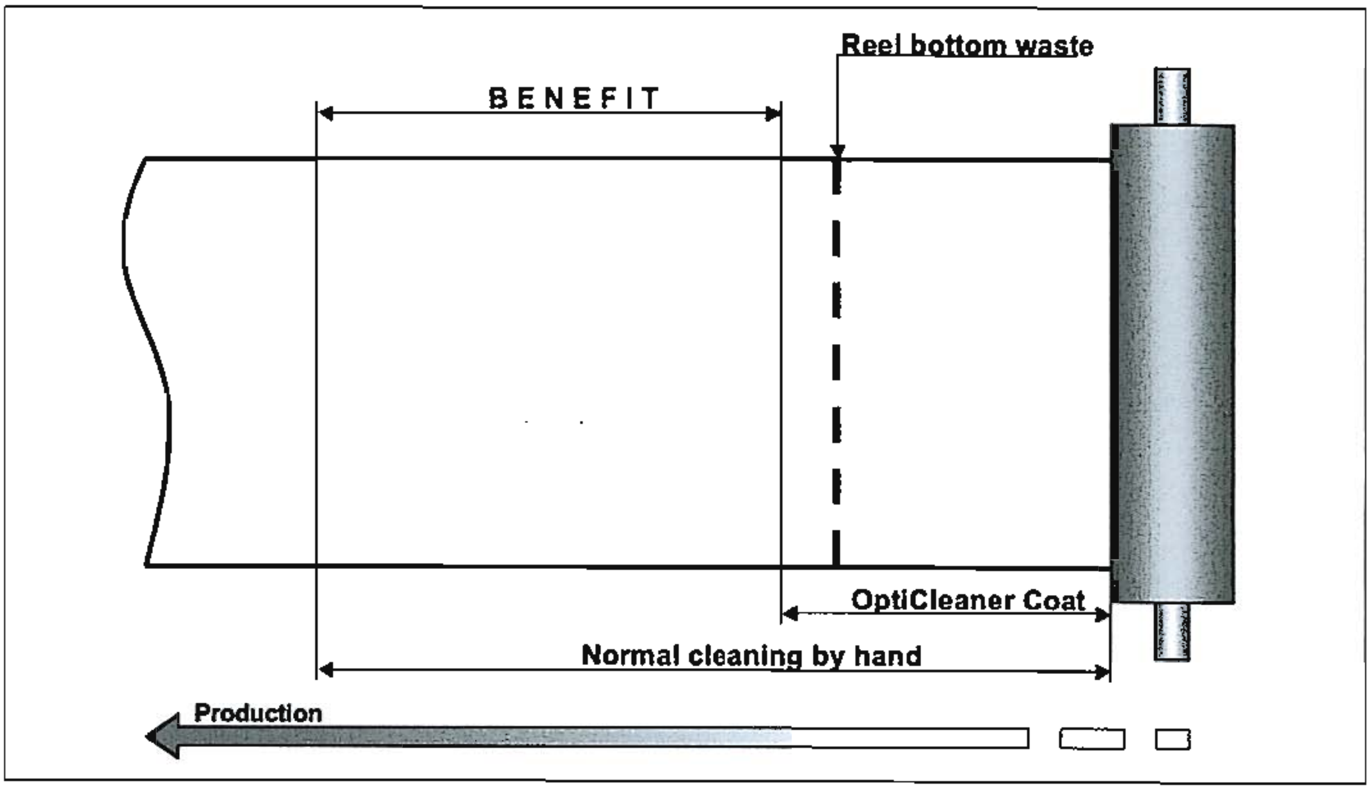

Figure 5 . Cleaning efficiency with automatic backing roll cleaner

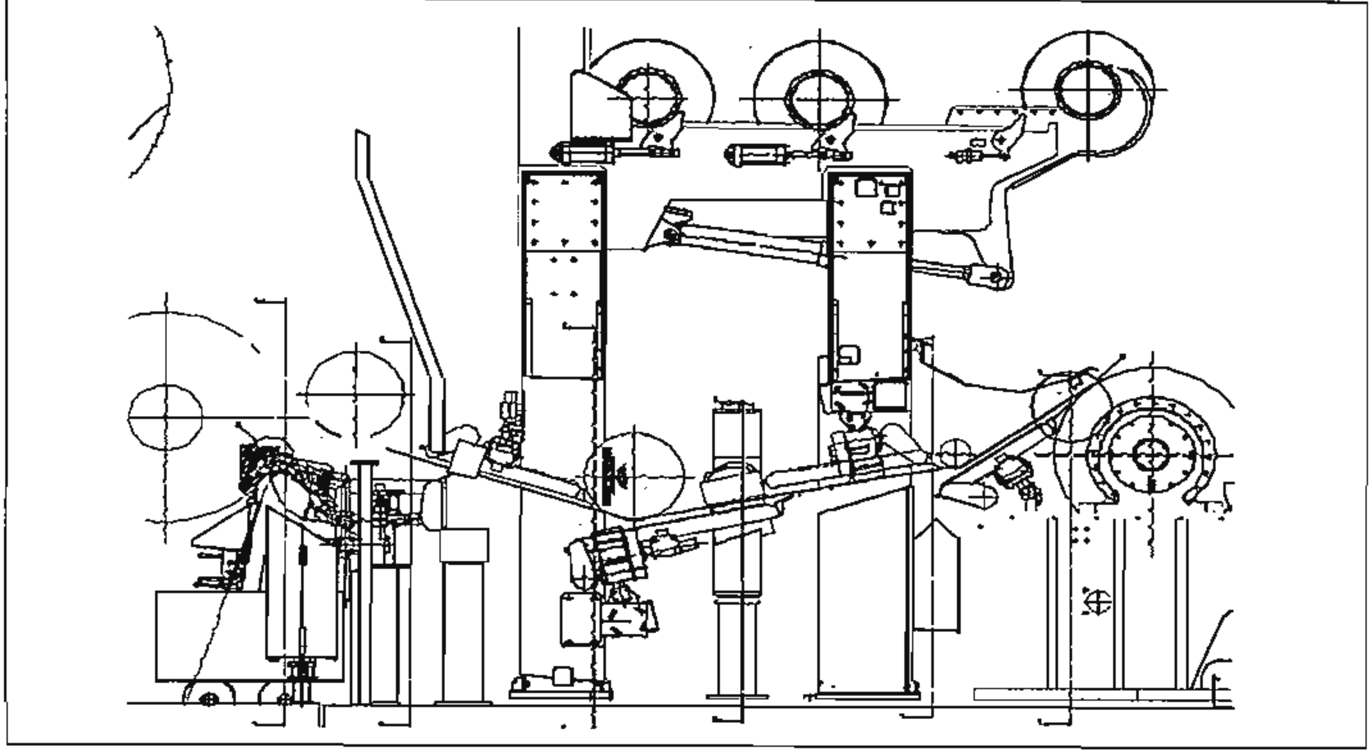

Figure 6. Tailor made tail threading solutions

*Production results*

A magazine paper production line was extensively rebuilt in order to increase speed and improve efficiency. In the past, tail threading inconsistency had been a major operational problem for the machine. Most of the breaks occurred in the coater sections of this on-line magazine paper machine. The tail threading system needed optimization in order to satisfy the demands for further speed increase and efficiency improvement.

A fully automated tail threading system with take-off devices were installed for the coaters and reel section. At the first coater, tail threading times after the rebuild have been reduced by 6 minutes per break from their previous best average threading time. At the second coater, break recovery times are approximately the same as those prior to the rebuild, although speed has been increased by 200 m/min.

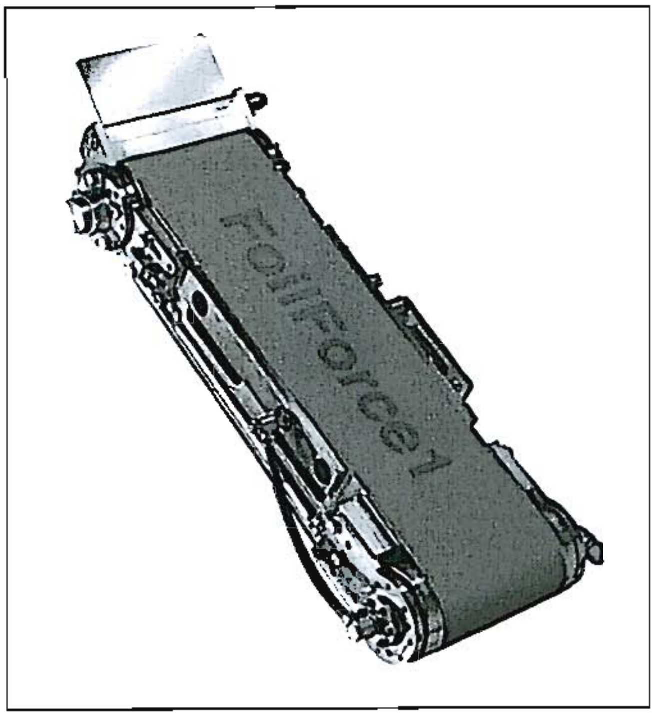

Figure 7. Ropeless tail threading device

## Conclusions

The efficiency and profitability of a paper or board making line can be significantly improved by various limited scope rebuild and upgrade solutions. A new machine is not always financially justifiable as a way to increase productivity!

With good maintenance, an existing line can be kept up and running. However, there is a clear limit where elimination of excessive maintenance costs can become the justification for a rebuild.

This paper presented some process improvements which positively benefit the efficiency and profitability of an existing production line:

- The productivity as well as quality potential of a coater can be enhanced by modifying and upgrading existing coating stations in many ways. For example, the coating stations can be equipped with new blade beams and automatic CD-coatweight profile controls.
- The automatic roll cleaning device reduces waste and improves safety in the coater area.
- A more functional tail threading system enhances the overall efficiency of the coating line.

The justified rebuild can consist of a correctly fitted single component upgrade, but more often involves a tailored combination of several such solutions. The installation can take place in one phase or in several scheduled phases to address issues related to quality, capacity or safety.

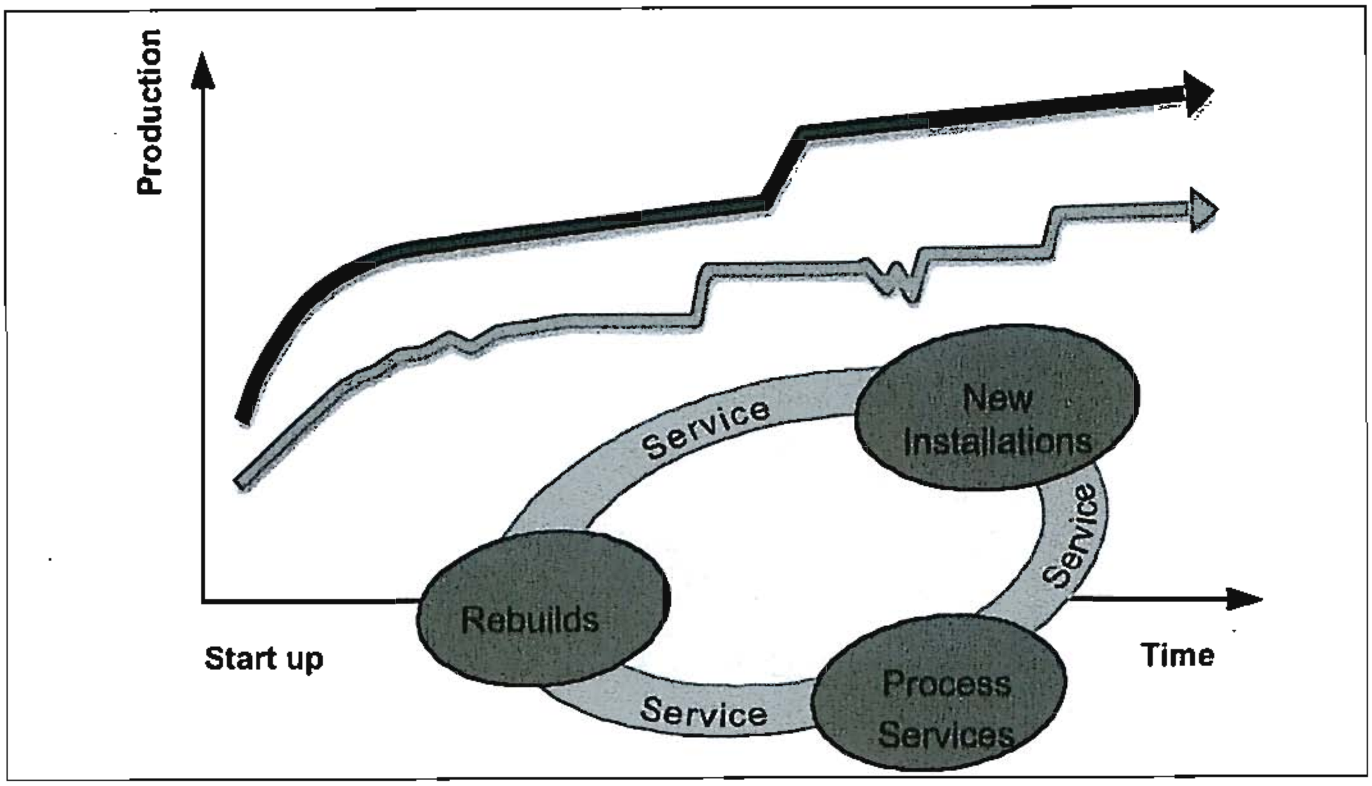

Figure 8. Continuous improvement for future success

# Blade Technology – a Tool for Improved Print Quality

by
**Kenneth Fagrelius**
BTG Duroblade S.A

SESSION ONE
PAPER TWO

## Abstract

In today's competitive world, the print shops require higher and more even paper quality.

The requirements differ from print process to print process but in general the demands are increasing.

Parameters to improve are:

- Runnability in the print process
- Paper roughness/smoothness
- Ink absorption
- Print gloss
- Visual defects.

Blade technology has made vast progress during the last 3 - 4 years; traditionally the material used was steel enhanced with aluminum oxide-based ceramics but increased demands for better coating quality, longer lifetimes and increased productivity, already at the paper/board mills, have pushed the development forward.

Today, we have a wide range of blade materials at our disposal, suitable for different processes in the industry:

- Chromium-based ceramics
- Metal-based materials
- Elastomer-based materials.

In this paper we will show that by simply changing the coating blade material we can largely improve quality when it comes to streak frequency, gloss increase and roughness decrease.

The materials have different characteristics but one common denominator is that the wear rate is much lower than that of a standard steel blade, which gives the papermaker the freedom to work with the tip geometry.

We will also show that modifications in tip geometry can substantially change the quality aspects of the finished paper, e.g. with small modifications the papermaker can simulate bent mode when running in stiff mode.

## Introduction

Since 1985, when BTG Duroblade introduced the first ceramic-tipped coating blade, until the beginning of the new millennium, blade technology focused on development of the existing base material, i.e. aluminum oxide. Different improvements of the material was made over the years and these ended up in improved blades, mainly focused on decreasing in the surface roughness of the blades. The blades were successful at the mills because of improved lifetimes and stable quality over time. However, the blades had their limitations; one being that the blade had a tendency to give the papermakers an increase in so-called micro-lines *(Figure 1)*, due to the roughness of the material of the blade tip. These, micro-lines were especially frequent when coating board in top coaters, and were not accepted by the mills and the end-customers, the print shops. When coating fine paper, the micro-lines mostly "floated out" in the drying phase after the coaters and were therefore not visible after the reeling. This was accepted by the mills as it engendered a decrease in unnecessary stops related to worn steel blades, savings on broke as well as the fact that an increase in production was possible.

The advent of new materials, such as chromium-based ceramics, metal- and elastomer-based materials has boosted blade use the last four years and the mills can today choose more precisely the blade suitable for each different process and quality, such as board, fine paper and LWC. This development has given a tool to the mills that allows them not only to focus

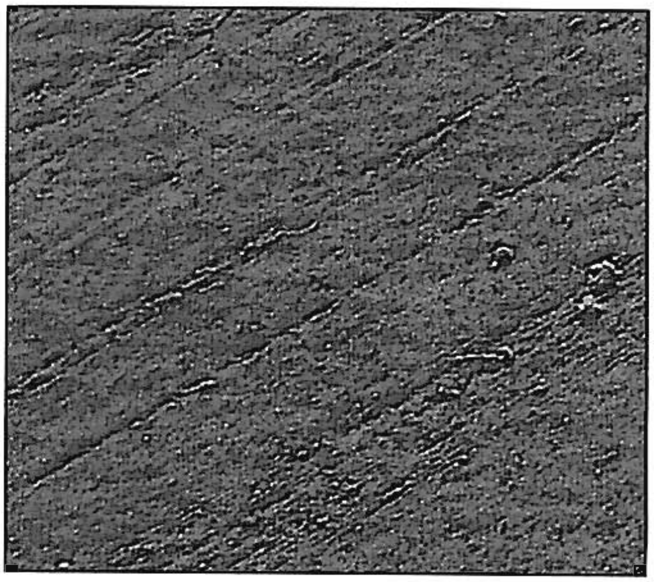
Figure 1 Microlines

on increased lifetime but also to choose a blade that will give them the possibility to improve surface quality and better reply to the increased demands of the print shops.

Another development is the double-beveled blades, which are very useful for different reasons when running stiff-mode and in some special configurations, when running in the grey zone between bent mode and stiff mode. This grinding technology requires a tough high-performance blade material to ensure that the second bevel comes to use and that it isn't worn out after a short time.

## Materials:

**Chromium-based ceramics:**

This material is part of the ceramic family. However, it has chromium oxide instead of aluminum oxide as its base. With the right blend you get a more homogenous and tougher material. This blade material has opened up the market of fast machines running under abrasive conditions, where the speed is high and low coat weight is applied.

LWC single-coated is a grade where historically most high-performance blades have failed due to the high wear rate of the aluminum oxide blades, hence the use of the blades could not be economically justified. With chromium-based materials the chances to succeed are greater thanks to the lower wear rate. Combined with double-bevel geometry the blades keep the original geometry for a longer time and the quality is more stable over time.

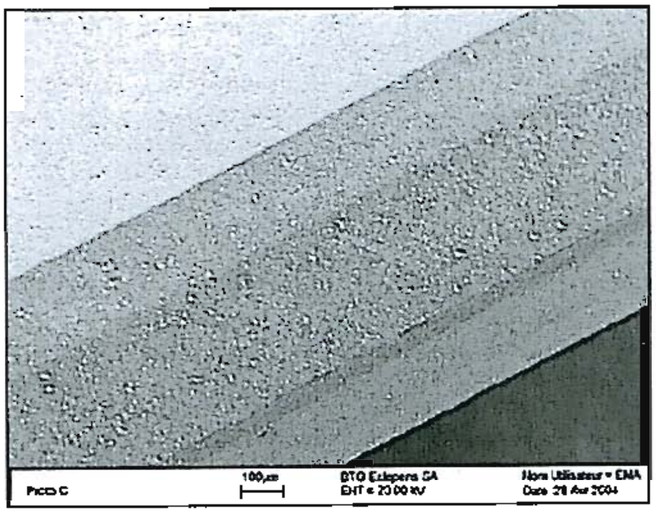

Figure 2 Chromium-based ceramics

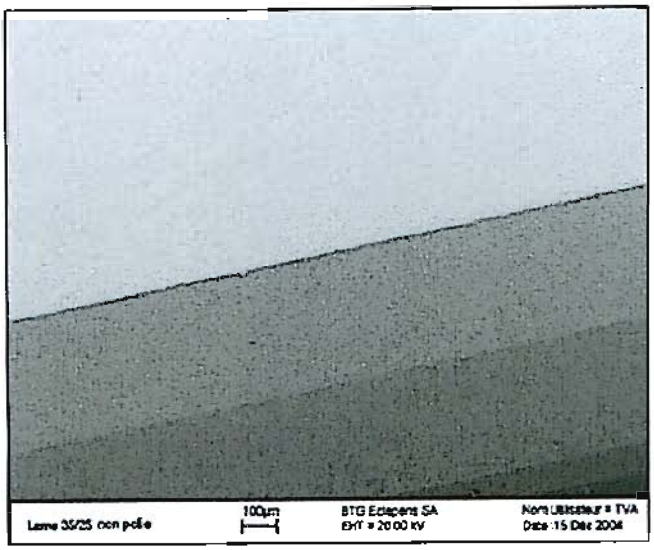

Figure 3 Metal-based materials

**Metal-based materials:**

This family consists of metal-based materials and the production technique is different. The surface of the blade tip is smooth and homogenous. Compared to aluminum oxide ceramics, it gives a reduction in streaks and scratches on almost all coaters were it has been run. The material is tough and wear-resistant, the blade keeps its original geometry over time and stable quality is achieved.

The main benefit with metal-based blades is the increase in paper gloss; the low surface roughness and the even wear results in low friction between the blade and the paper, enhancing a smoother flow under the blade, which improves the pigment orientation.

The drawback with metal-based materials is that they are sensitive to dry friction on some machines, when running at high speeds.

A typical configuration in a board machine is a tougher metal compound on the pre-coaters for longer lifetimes and a finer compound on the top-coater for excellent quality and a decrease in streaks and scratches.

If we compare aluminum oxide with the new materials, we can clearly see that the surfaces are more dense and homogenous. The roughness is very low on the metal carbide surface compared to the ceramics.

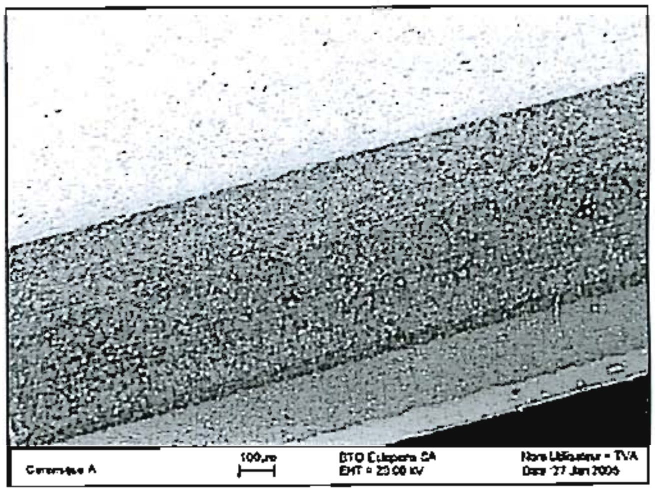

Figure 4 Aluminium Oxide ceramic

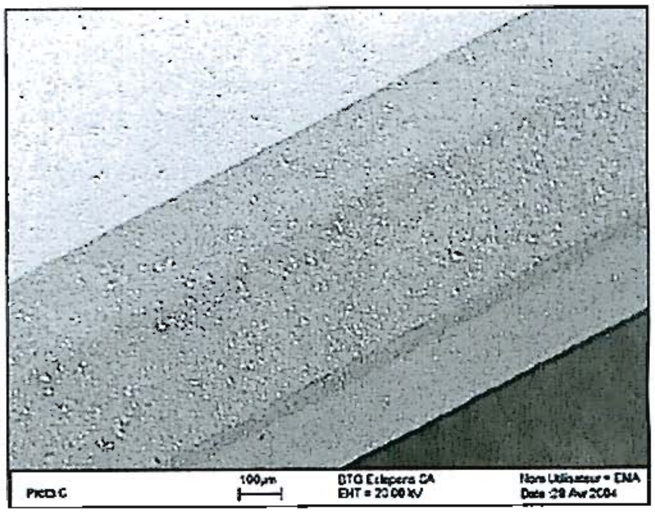

Figure 5 Chromium Oxide ceramic

**Elastomer-based materials:**

This blade type consists of a steel strip with an elastomer edge that has a soft and compressible blade tip, which better follows the paper topography. The fibre coverage is superior to that of all other coating blades today and the soft material is actually very wear- resistant. The drawback with soft-tip blades is that they are very sensitive to dry friction and require lubrication., however, when well lubricated with coating colourwe can hardly see any wear on the blade, even after very long running times.

As mentioned, the main benefits are superior fibre coverage and even paper smoothness in the CD direction over the web.

## Multibevel concept:

### The basic differences between running bent blade mode and stiff blade mode:

When running in bent blade mode you work with low angles, e.g. 5° and the hydrodynamic forces under the blade tip dominate, while when working in stiff blade mode you work with high angles up to 50° and the contact pressure is the dominating force.

**Bent blade mode:**

Bent mode is suitable for machines running up to 1,000 mpm and with high coat weights. Higher speeds normally give too high hydrodynamic forces under the blade tip and it becomes hard to control the coat weight.

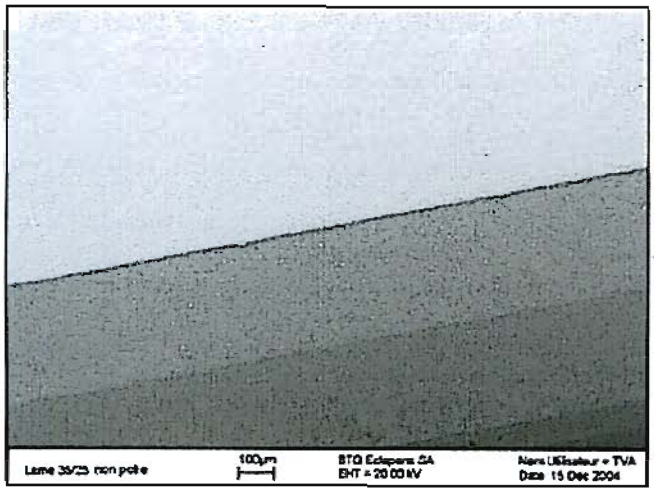

Figure 6 Metal carbides

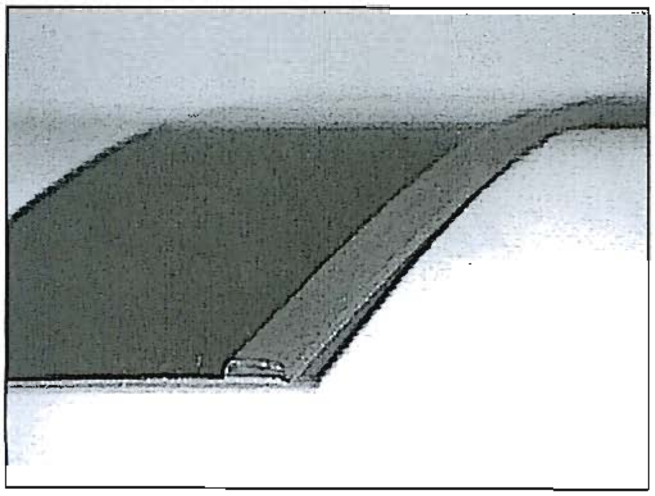

Figure 7 Elastomer-based materials

The coating colourflow under the blade is high due to the narrow space between the blade and the paper, the turbulence at the blade is low and the dewatering zone is long, which favors a better alignment of the coating pigments parallel to the base paper, the pigment particles having time to orient properly *(see Figure 10)*. The pigment orientation gives an increase in gloss; and the fibre coverage is better when running in bent mode because of the blade's ability to follow the structure of the base paper. However, the flexibility of the blade makes the profiles harder to control.

**Stiff blade mode:**

Stiff mode is more suitable for faster machines running with lower coat weights.

When running in stiff mode the dewatering phase is abrupt, the coating colour excess is doctored off and the flow under the blade is lower due to higher angle against the web. The turbulence and mixing of the coating colourat the blade limits the time for the pigment particles to orient properly and gloss is normally lower *(see Figure 11)*. The blade doesn't follow the structure of the fibres, which results in lower fibre coverage. The profile control is easier thanks to less bending and flexibility of the blade.

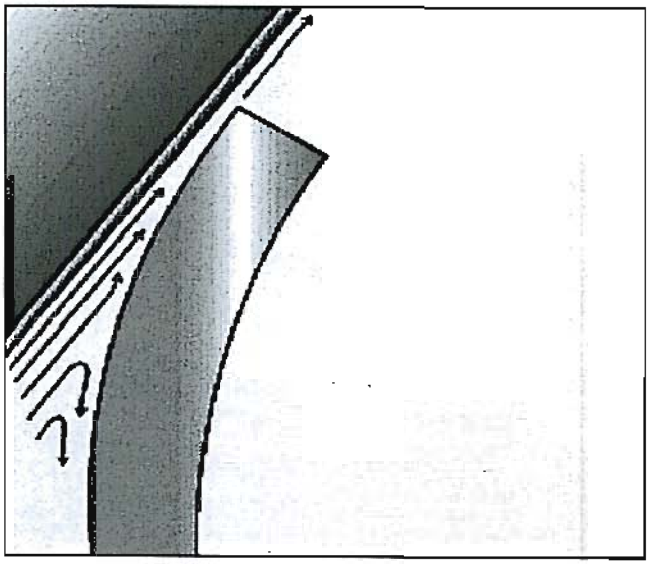

Figure 8 Low-angle, bent mode

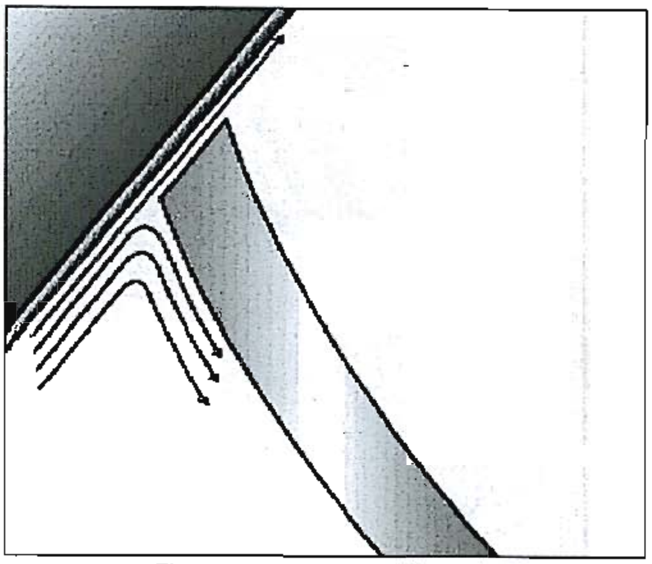

Figure 9 High-angle, stiff mode

Which mode is chosen, is the paper maker's decision and as shown above there are both negative and positive effects for both methods. In some cases, it is not possible to run in bent mode, namely - as mentioned before - when the machine speed is too high or when the coat weight is too low.

**Double bevel concept:**
This is a development mainly aimed at papermakers running in stiff mode and who cannot, or don't have the intention to, run in bent mode but who would like to increase the quality or run ability of the coaters.

When running a traditional steel blade in a coater we know that the wear rate is high. We also know that a steel blade is much more forgiving then a high-performance blade. When working with a steel blade the run-in time is short due to the fact that the blade wears and shapes to the conditions fast and the profiling is easier in the beginning of the run. With a high-performance blade the wear is much slower, hence it is important to find the right blade tip geometry from the beginning. Most coaters are not perfectly straight in the CD direction; with a steel blade this is not a problem but with a blade with much lower wear rate this could easily cause profile problems because the blade will run on the heel in some positions. That is why, when you grind a second angle on the blade, you move the sharp heel further from the paper and the risk of running on the heel is much lower.

The benefits of the double bevel blades are the short run-in time and the forgivingness of not completely straight coaters, (less sensitivity to the straightness of the coater). Other benefits more focused on the quality are:

- Good and stable profiles
- Fewer blade scratches
- Increased gloss
- Increased fibre coverage.

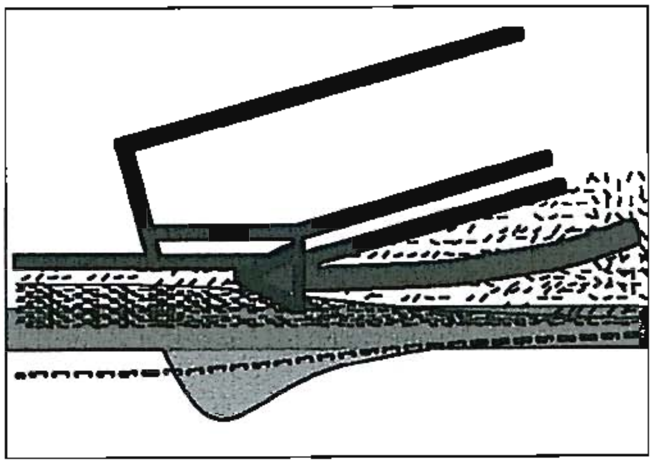

Figure 10 bent blade mode

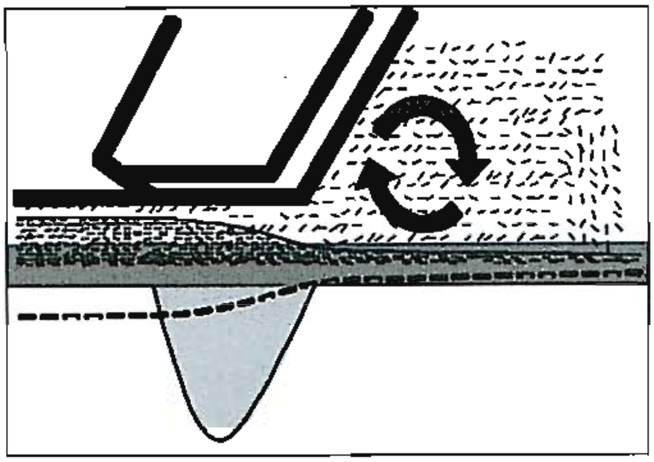

Figure 11 stiff blade mode

The second bevel prolongs the dewatering zone and gives the pigment particles the proper orientation, which results in increased gloss. The fibre coverage improves thanks to the increased flow under the blade, which gives the coating colour the ability to follow the structure of the base paper. Generally speaking, we can say that we increase flow without bending the blade too much and that the contact pressure is reduced *(see Figure 12)*.

The risk for scratch/streak problem is greater when running in stiff mode. In bent mode operations, the flow has a tendency to push the impurities under the blade tip. With a double bevel the wedge between the blade and the paper opens up, which gives the impurities a greater chance to pass under the blade while the increased flow helps pushing them under the blade tip.

## Conclusion:

With the new materials and improved understanding of what happens under the blade tip, papermakers can now also focus on the quality parameters and not only concentrate on the lifetime when using a high-performance blades. Obviously, the high-performance blade is more expensive than a traditional steel blade and some sort of payback is necessary. When talking about cost savings we need to consider other parameters than purely an increase in lifetime. Below are some examples of papermakers using the new materials for other reasons.

- Reduction of scratches when using a double bevel metal-based blade. Savings on broke and claims.
- Even roughness quality in the CD direction when using an elastomer-based blade. Savings on broke.
- Increased solids level when using a chromium/ceramic-based blade. Savings in drying energy and higher flexibility to make improvements in the coating colour.

The demands will continue to increase and blade suppliers need to continue developing and increasing their knowledge of what happens under the blade tip. These new observations described here are a good and stable base for further developments.

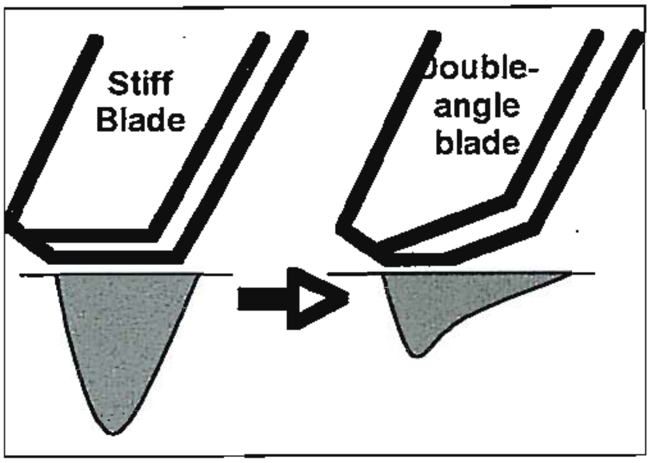

Figure 12 Dewatering zones

# Free Jet Coating Application – Recent Experiences with "Closed Head" Design

*by*
**Paolo Rabito**
PMT Italia

SESSION ONE
PAPER THREE

## Introduction

The advantages of the free jet coating application are well known; the report aim is to discuss the free jet coating application characteristics through the S-FLOW "closed head" design, developed by Mitsubishi Heavy Industries.

The used concept, different from the "conventional" open type, assures a more stable, homogeneous and repeatable in time jet structure; in addition it is very flexible and reliable for the different production requirements, such as different coating types, machine speeds, basis weights and sheet surface characteristics.

Before analysing the results of coating application with closed head, it is important to understand the technical-structural characteristics, that make this system stable, versatile and reliable in time.

*Figure 1* shows the stainless steel body assembly; at the upper end there are two lips that convey the jet to be applied on the paper. One lip is fixed, while the other one is adjustable through set screws.

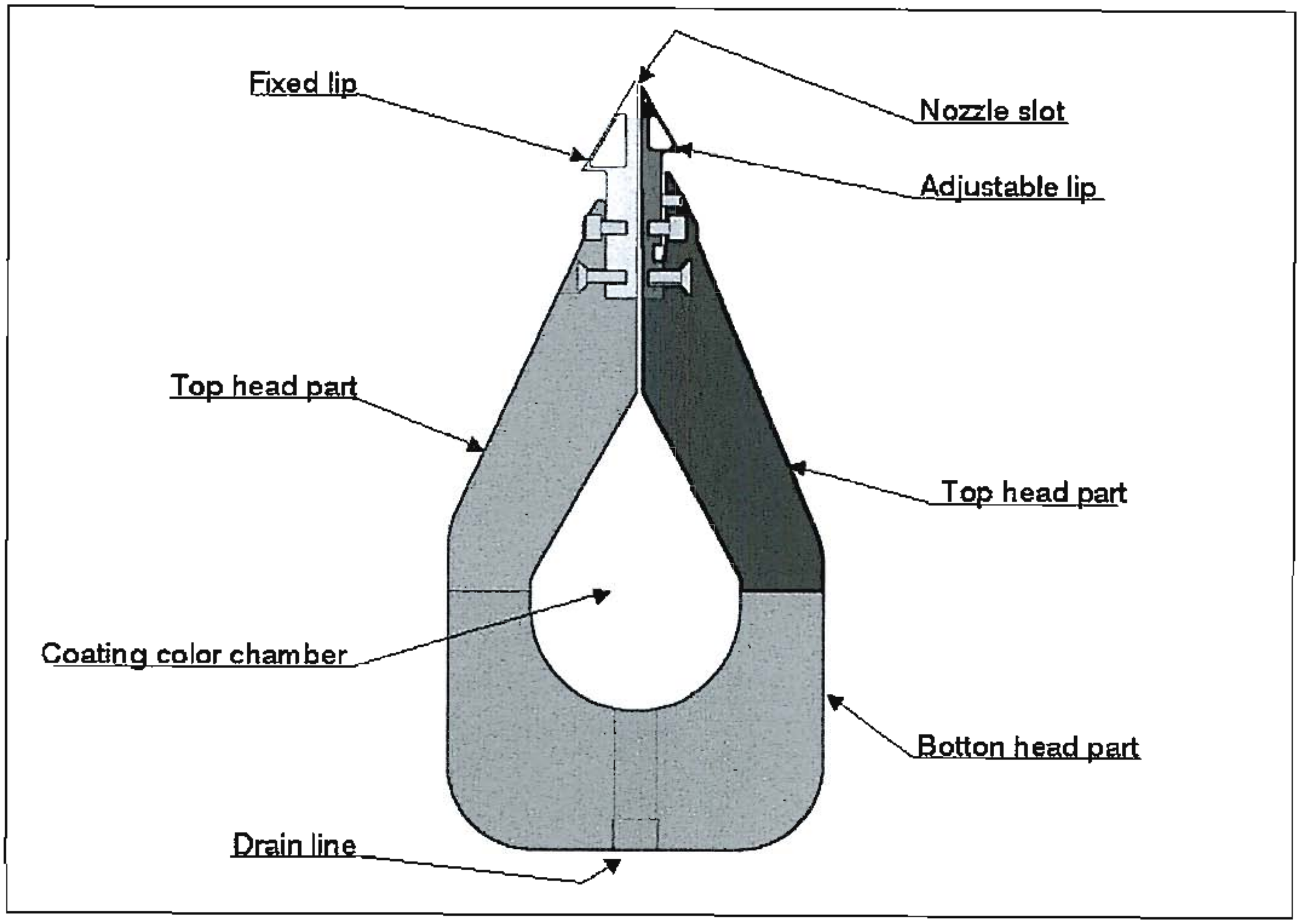

Figure 1 Free jet lips and head design

Thanks to the symmetrical coating feeding from both end sides *(see Figure 2)* and to the free jet design, the coating colour on the paper and subsequently the applied film is always stable and uniform, allowing constant operating conditions.

*Figure 3* shows a simulation of coating velocity inside the free jet chamber: the absence of "dead zones" avoids the coating waste production.

The filters *(see Figure 4)* installed at both ends of the free jet avoid the passage of possible coating grumes, eliminating the possibility of disturbing the jet during machine operation.

In order to have a stable nozzle structure, the lips and the free jet body are equipped with cooling chambers. They keep the system clean during operation *(see Figure 5)*.

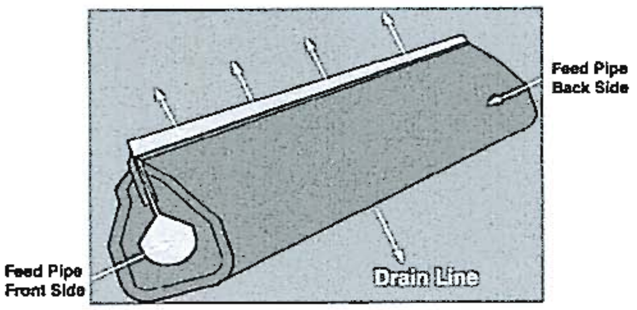

Figure 2 Free jet head feed system

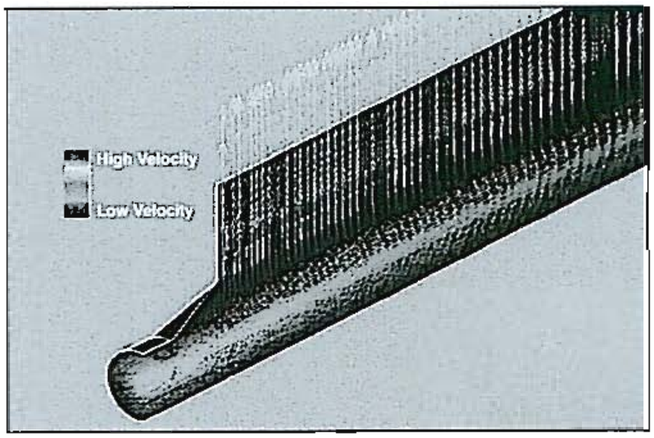

Figure 3 Free jet velocity distribution

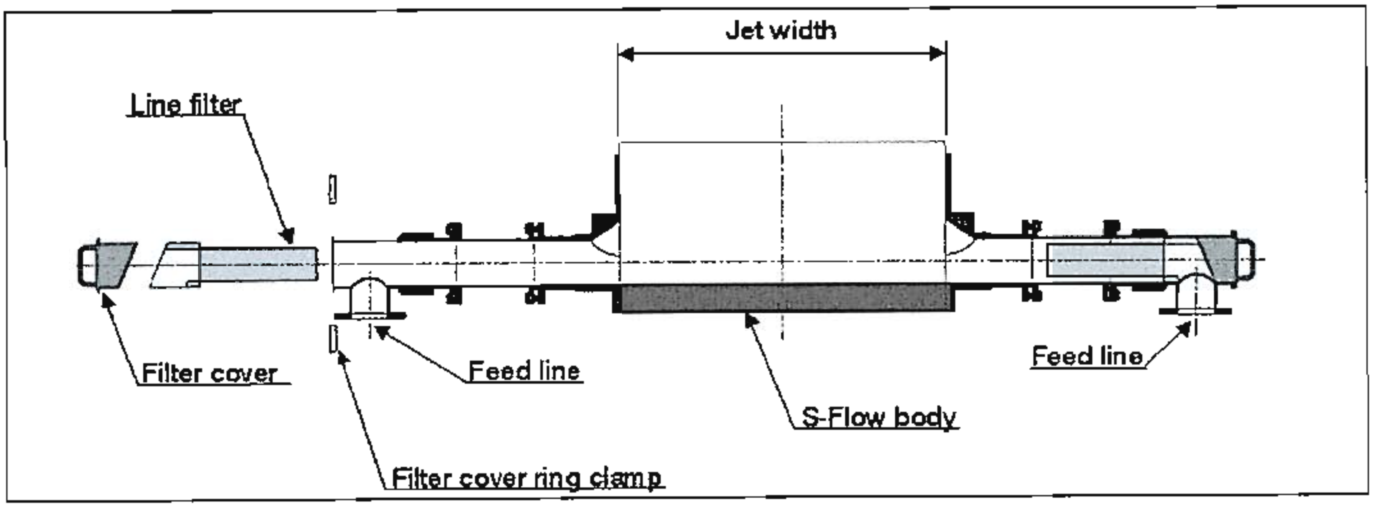

Figure 4 Free jet filters & head design

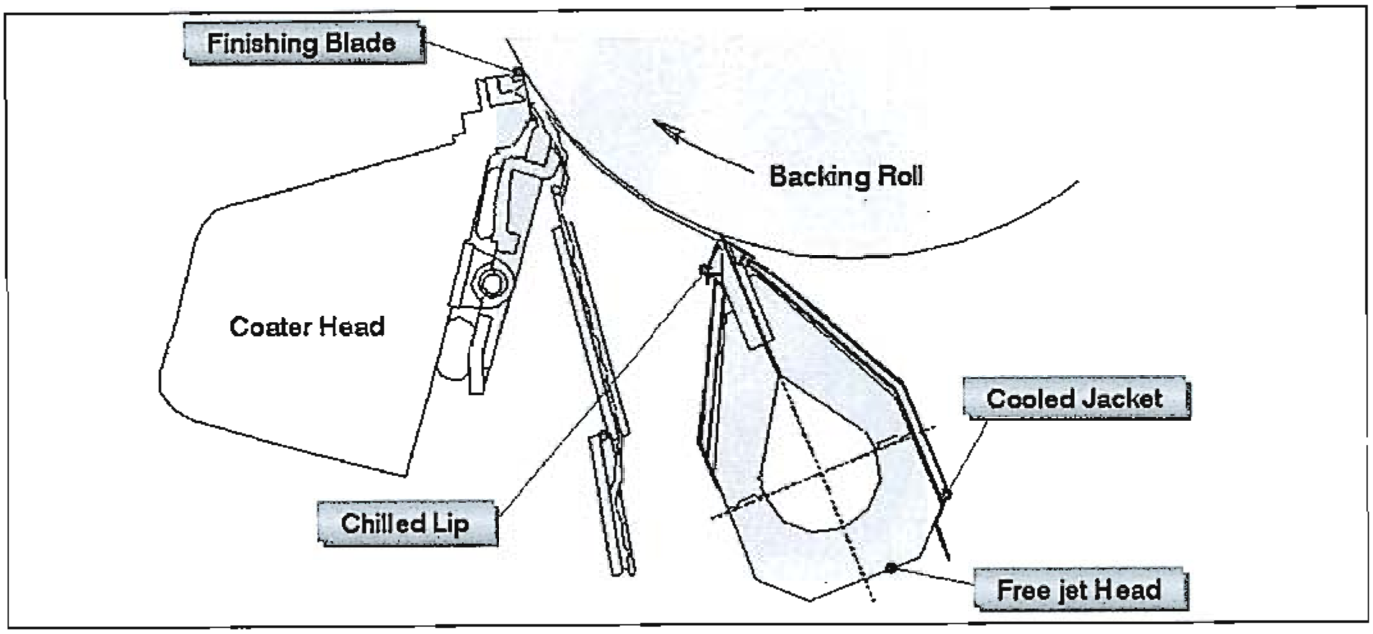

Figure 5 Free jet cooling system

*Figure 6* shows the parameters defining the nozzle structure and position compared with the backing roll. As the lips are fixed and straight, it is possible to adjust the nozzle opening from 0.8 mm to 1.5 mm, acting as for adjusting the headbox lip. The distance from the backing roll can vary from 5 to 15 mm.

*Figure 7* describes the importance of the angle produced from the coating jet and the paper. This adjustment possibility is very important to obtain a constant jet and subsequently a good coating application quality according to the machine speed, to the coating formulation and to the paper surface features. The angle can vary from 40° up to 65°. The change of the jet angle in relation to the backing roll is guaranteed by two mechanical jacks operated by electrical engines.

The uncoated edge is guaranteed with high precision through provided devices *(see Figure 8)*.

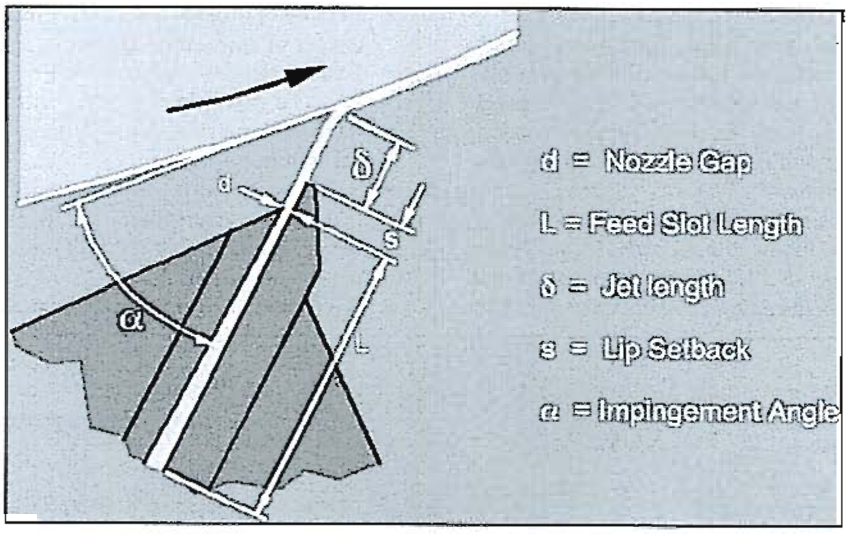

Figure 6 Free jet nozzle geometry

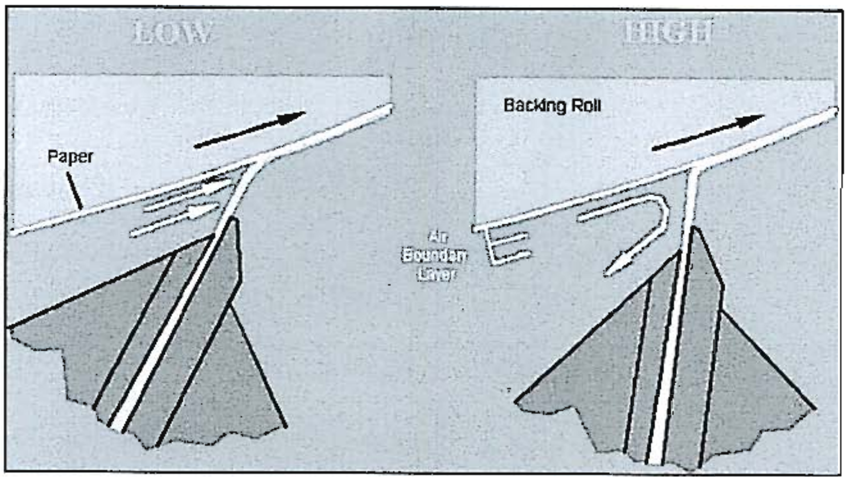

Figure 7 Free jet angle impingement

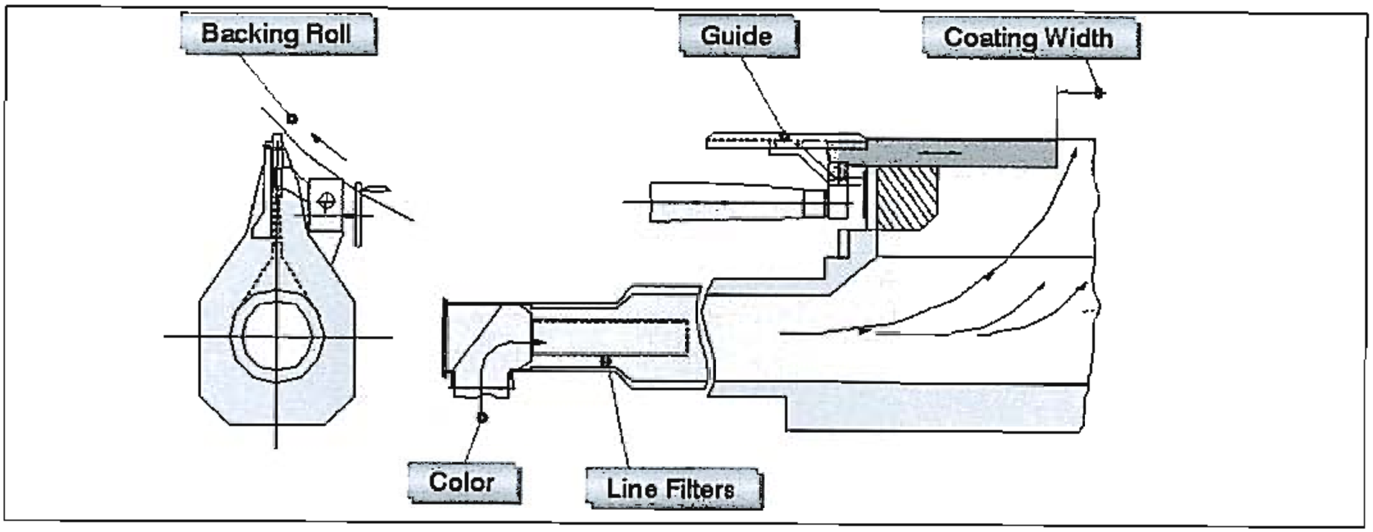

Figure 8 Free jet seals

*Figure 9* shows the free jet installation on its whole. Hydraulic cylinders and a lever system allows the body to move from a waiting position to a working position or to a maintenance and cleaning position.

In *Figure 10* the parameters needed to obtain a stable jet and a good coating quality, without back flow or skip coating, are described. The optimisation of these parameters is performed by mill according to the different coating types, paper surface characteristics and machine speeds.

The experience achieved in Belgium demonstrated high flexibility. Using the same equipment it is possible to apply different coatings at different machine speeds. Target paper surface characteristics are also very different. Three years after the installation, no problems of dirt inside the closed body have been noticed during operation.

The experience in Italy is similar from the point of view of the flexibility and cleanness. In this case the application is even more critical because some of the coating formulation are absolutely not compatible. In the case of coating contamination the paper would be rejected from the quality control. Following the normal flushing procedure and using hot water, two years after the installation, no cases of obstruction or coating contamination have been remarked

## Conclusions

- The "closed head" design is simple to operate: few adjustments are required.
- Better jet profile and stability, even at high speed, reduce the danger of application faults.
- Easy to clean
- Reduced down time.
- Its symmetric structure with a straight nozzle makes it very accessible.
- The possibility to adjust the jet angle during operation makes it very versatile.
- Seal efficiency contributes to keep clean the equipment during the operation.
- Easy maintenance due to the simple design.

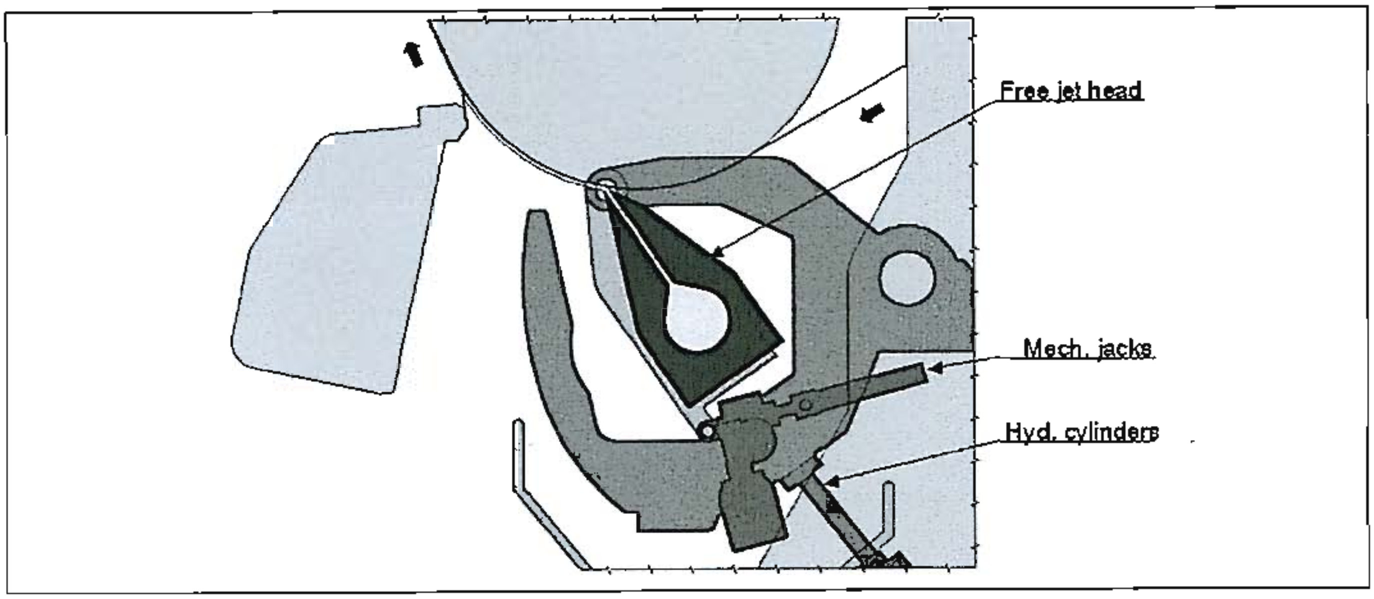

Figure 9 Free jet coater station

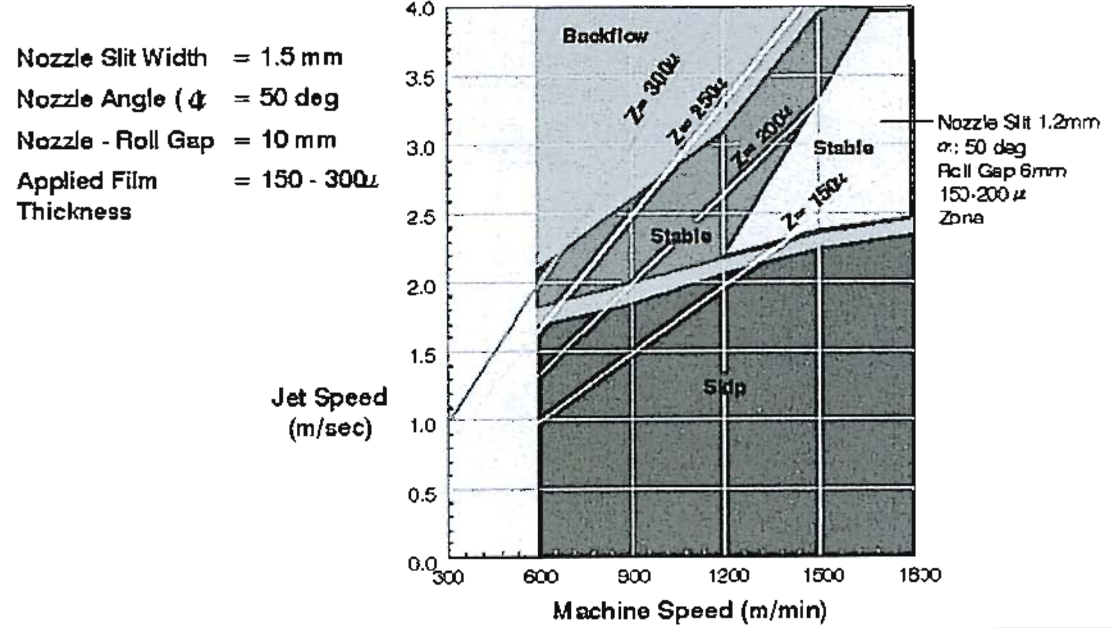

Figure 10 Stability zone of the jet

# New Technology to Measure the Parallelism of Rollers

*by*
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**Martin Hummel, Matthias Ecker**
Prüftechnik Alignment Systems GmbH

SESSION ONE
PAPER FOUR

The alignment of rollers is referred to as a special art. Well aligned rollers are vital to avoid wrinkles or tears in the materials involved in the coating or converting process. In addition, rolls in printing machines, a possible further production step, need to be parallel, if passers should fit. Production speeds have been continuously risen over the years, at the same time, material thicknesses are decreasing: there's an ever greater need for well aligned rolls.

This lecture presents a completely new procedure to measure the parallelism of rollers: It is based on the ring laser gyroscope technology as used for navigation in the aerospace industry. The measuring system developed by Prüftechnik Alignment Systems GmbH is called Paralign®, *see Figure 1.*

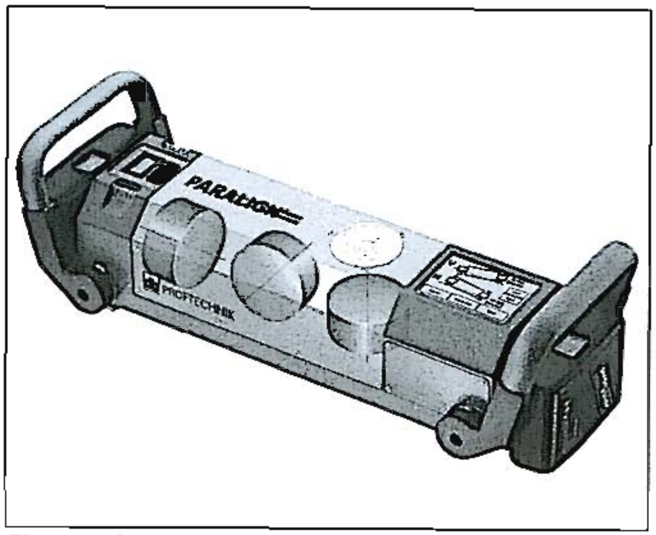

Figure 1: Paralign® device, containing three Ringlaser Gyroscopes

Conventional optical systems as e.g. theodolites require a lot of time to perform a measurement. The necessary optical line of sight from the machine axis to the rollers to be measured can sometimes only be obtained by means of additional mirrors and prisms. The repeatability of measurements is thus limited or the measurement is even impossible.

Measurements with Paralign®, however, can be performed within a fraction of time compared to traditional measurements - indeed for all rollers to be measured as no optical line of sight from the machine shaft to the rollers is necessary. Consequently the time required to measure rollers within housings - e.g. drying sections - is the same as for accessible rollers. Paralign in use at a converting line is shown in *Figure 2:*

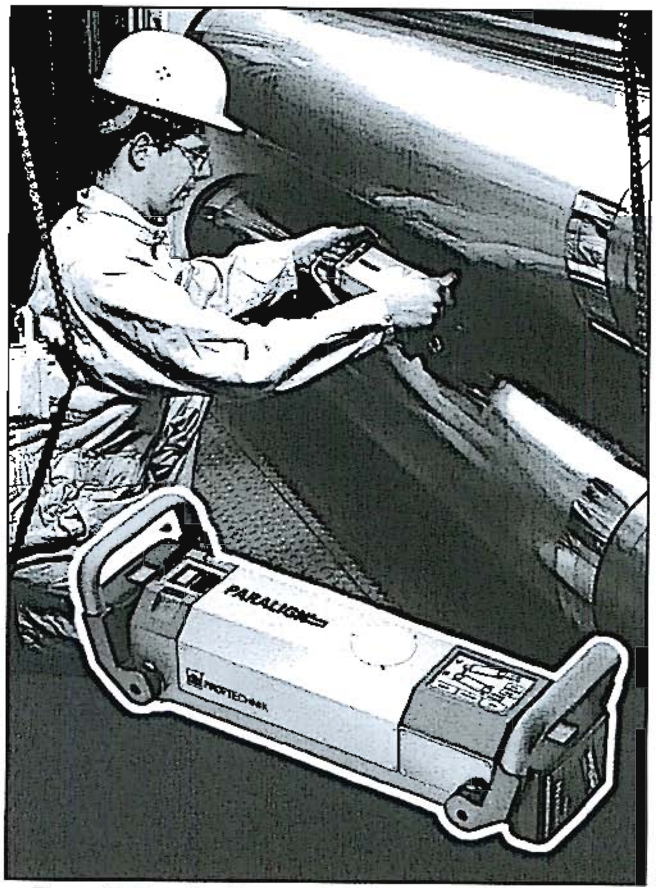

Figure 2: Paralign® measurement at a calender stack

# NOTES

# The Fourth P; Power. How to Save it to Make Money

*by*
**Tim Klemz**
Compact Engineering Ltd

SESSION ONE
PAPER FIVE

News of rising energy prices has become commonplace over the last year or so and increasing energy costs have been held responsible for the closure of several mills in the UK over the last 12 months.

Papermaking is an endemically energy-intensive process with large volumes of water requiring removal from both the substrate and any aqueous coating that is applied to the sheet surface. With high wholesale energy prices, the ever-present Climate Change Levy and distribution costs higher than elsewhere in Europe, now is an excellent time to invest in energy saving technology.

There are a number of methods of applying an aqueous coating to a sheet of paper or board and the coatings are applied for a number of reasons, normally either aesthetic or functional and commonly a mixture of the two. Technological advances are being made that allow the solids content of coating colour to be increased, thus reducing the drying requirements. The changes that are being made encompass both the physical equipment required for the application of the coating as well as the chemical components of the coating itself, where the rheology of the coating colour is modified to ensure good coverage.

Drying the water from the coating represents a critical phase in the production of the coated product. If the drying regime is wrong or performing poorly, the potential costs and subsequent implications on profitability can be dire. Failure to dry coatings effectively results in poor control of binder migration, which in turn results in poor printability and a reduction in the visual impact of the coated product. While sub-standard product can be returned to the broke pit so that some raw material can be recovered, the cost of the lost added value and machine time cannot be recovered and in a competitive marketplace operating on thin margins, not many mills can afford to manufacture sub-standard product for long.

Modern coating lines will generally incorporate a number of different drying methods. The choice of drying system will depend on the product being made, the coat weights, line speed and purchase and running costs.

A common combination of drying types is infrared followed by either hot air dryers or drying cylinders, with cylinders being more prevalent on on-machine coaters.

In this paper we will look at the operation of the Titan short wave infrared dryers from Compact Engineering and the running cost reductions that Äänekoski Paper Mill witnessed as a result of removing their existing short wave infrared dryers and replacing them with Compact Engineering Titan dryers and making some improvements to the operation of their hot air dryers.

We will start with a brief introduction to infrared and some of the physics that determines the properties of infrared and we will then look at the Titan dryer and how the design of it combines the benefits of high-intensity infrared with an active boundary layer management system to provide an efficient means of mass transfer. We will also look at the role that infrared plays in the chosen drying regime and examine some results from Äänekoski and then draw some conclusions.

## Infrared: A brief introduction.

Infrared is a small yet significant part of the electromagnetic spectrum sandwiched between microwaves and visible light *(Figure 1)*. The infrared area of the electromagnetic spectrum is further sub-divided into three distinct bands of infrared,

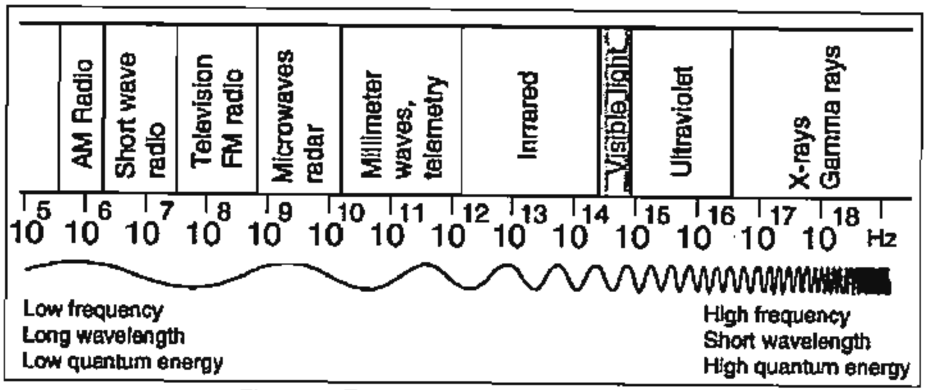

Figure 1. The electromagnetic spectrum

identified as long wave medium wave and short wave (or far, mid and near IR) with the distinction between each band being determined by wavelength *(Figure 2)*. The temperature of the emitter determines the wavelengths of infrared, with the hottest emitters producing the shortest wavelengths and consequently the highest energy densities. As a result of this, it is only the medium and short wavebands that are of interest to paper makers as they are capable of transferring the maximum amount of energy per unit area and we will focus on the application of short wave infrared.

The total radiant heat from an emitter is calculated using the Stefan-Boltzmann Law that is essentially an integration of Max Planck's Law for emissions at all temperatures. The Stefan-Boltzmann Law states that the radiant heat from a body with an area $A = A \times \epsilon \times T^4 \times \sigma$

Where $\epsilon$ is the emissivity of the emitting body,
$T$ is the absolute temperature of the emitting body and
$\sigma$ is the Stefan-Boltzmann constant = $5.67 \times 10^{-8}$ ($Wm^{-2}K4$)

It can be seen that the temperature of the emitter has a profound effect on the total energy emitted and if the wavelength of the radiation being emitted was not important then the optimum lamp design would be one that ran at the highest possible temperature. However, wavelength plays a vitally important role in heat transfer by radiation as heat transfer by radiation occurs when the frequency of the incoming electromagnetic wave is the same as or close to the natural resonance of the inter-atomic bonds within the structure being heated. The closer the match between the emission frequency and the absorption characteristics of the solid being heated then the radiation is more readily absorbed and less of the emitted output is either reflected or transmitted.

The relationship between the absolute temperature of the emitter and the peak wavelength of emission, $\lambda_m$, is given by Wien's displacement law, where $\lambda_m T$ = constant. If $\lambda_m$ is expressed in microns then $T\lambda_m = \underline{2898}$ Therefore, if an emitter has a running temperature of 2450K then the corresponding peak wavelength will be 2898/2450 = 1.18μm as is the case with commercially produced lamps.

Short wave infrared is that part of the electromagnetic spectrum that occupies the waveband between 0.76μm and 2μm corresponding to emitter temperatures of between 3800K and 1450K and it is always generated using tungsten-halogen lamps that use electricity as an energy source.

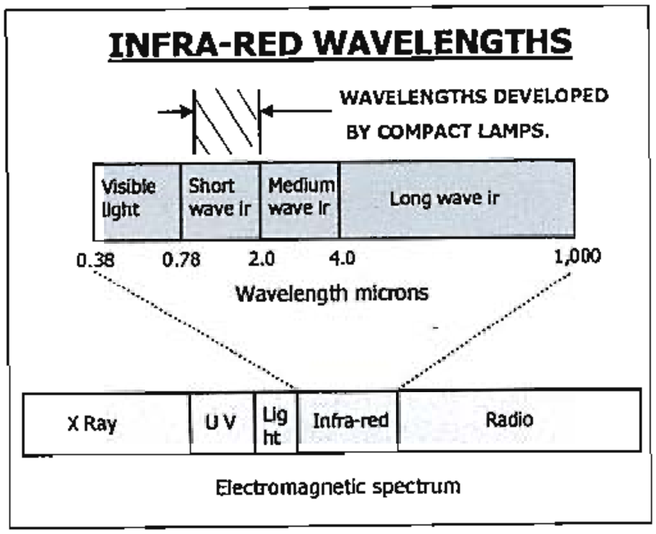

Figure 2. Wavebands of infrared

Tungsten is used as it is capable of withstanding the high temperatures demanded in generating the shorter wavelengths of infrared radiation and the halogen is added to prevent the tungsten that is evaporated from the filament from condensing on the inside of the quartz tube.

Bearing in mind the relationship between the wavelength of the radiation and the absorption characteristics of the solid being heated, it is important to generate wavelengths of infrared that are going to be absorbed by the cellulose fibre in the sheet and the components in the coating colour. Neither cellulose fibre nor most coating ingredients will absorb any radiation that is shorter in wavelength than 1.30μm so generating shorter wavelengths of radiation is expensive and wasteful.

At Compact Engineering, we manufacture our own emitters that are specifically designed to transfer energy to the heart of the sheet and they work at a temperature of 2150K producing a peak wavelength of 1.35μm. The choice of 1.35μm as a peak wavelength is so that the energy is able to penetrate deep into the sheet structure. If the wavelength were any shorter, too much energy would pass straight through the sheet. Generating the correct wavelengths of infrared is important when drying coatings as the infrared has two functions to perform. Firstly, it is required to increase the vapour pressure in the sheet structure and secondly, it is required to heat the water in the coating. The water in the coating will preferentially absorb medium wave infrared with a wavelength between 2μm and 4μm and over 80% of the energy is absorbed in the first 20μm of the film thickness.

On sheets where the combined thickness of sheet and coating is less than 20μm, medium wave infrared generated by burning gas is an acceptable source of heat. As the sheet thickness increases, the proportion of shorter wavelengths has to increase to penetrate the sheet. Failure to heat the sheet results in their being too little resistance to the water in the coating that will move in to the sheet as it is warmed and its viscosity reduced.

The unique lamp design allows the optimum wavelengths of infrared to be generated while running the emitters at either 2kW or 5kW each depending upon both design and requirements.

*Table 1* below, shows the importance of running emitters at the correct colour temperature to ensure the generation of the preferential wavelengths of infrared. In the above table it is possible to see that there is a large proportion of energy that is available to be absorbed by the cellulose fibre in the sheet and the components in the coating colour from the energy emitted by the Compact Engineering lamps. In fact, just over 75% of the total emissions from an emitter running at 2150K (1.35μm) are available to be absorbed by the sheet compared to around 60% from the industry standard lamp running at 2450K (1.18μm). The shorter wavelengths are not only unavailable to heat the sheet as they are transmitted but they are expensive in kilowatt terms to generate, as they are higher energy waves.

| Wavelength range (μm) | % Of total energy at 2450K | % Of total energy at 2150K |
|---|---|---|
| Short of 1.4 | 41 | 31 |
| 1.4 to 2.5 | 37 | 42 |
| 2.5 to 3.6 | 14 | 17 |
| Long of 3.6 | 8 | 10 |

Table 1 Percentage of total output at different wavelengths for emitters running at different temperatures for a 2kW lamp.

Increasing the proportion of emitted energy that can be easily absorbed by the sheet is clearly of interest, but there are other considerations to be taken into account, especially when drying coatings. The fact that the frequency of the incoming wave does not have to be a perfect match for absorption to take place can be used to great advantage. Generating infrared from an incandescent source results in a relatively broad waveband of infrared being emitted rather than a single wavelength. This in effect means that the coating and substrate are heated and the coating is effectively dried from the interface between the sheet and the coating. This is beneficial for the control of binder migration and we will look at this again later in the paper.

## The Titan dryer

The Titan has been specially designed for modern high-speed coating applications. It is capable of applying a large kilowatt density to the sheet, with each frame being able to apply 333kW/linear metre, which is the equivalent of 530kW/m². The Titan uses special 5kW lamps that have a heated length of 600mm and the total machine direction length of the dryer ranges between 780mm and 850mm depending on the air handling system used.

Generating the correct wavelengths of infrared is just the start of successful drying. Coating colour is formulated to reflect light so that the printed image is shown with the best possible definition. This is great for aficionados of the printed image but rather bad news for manufacturers of infrared dryers who want the coating and the underlying sheet to absorb their infrared. Infrared, being closely related to visible light behaves very much like visible light and is reflected by many of the same elements. Thus ingredients in a coating colour, such as titanium dioxide, that are included because of their reflectivity of white light, increase the reflectance of infrared too.

To compensate for this high degree of reflection from the surface of the coated sheet, it is important that the design of the infrared dryer takes this possibility into consideration.

The Titan dryer benefits from a series of planar reflectors that are set behind the lamps. The reflector bodies are coated in a special gold formulation that exhibits superb reflection characteristics of infrared and they are angled to maximise absorption by the coating. This reflects the radiation back to the sheet at the original wavelengths until absorption takes place.

The reflectors behind the lamps ensure that the majority of the primary radiation is presented to the sheet at as close to 90° as possible as this enhances the rate of absorption. Careful management of the reflected radiation and using reflectors to direct the primary radiation towards the sheet so that the optimum incident angle of 90° is maintained can increase the overall efficiency of an infrared dryer. A typical sheet will reflect as much as 60% of the radiation initially presented to it, but the energy used to generate this radiation need not be lost from the overall drying equation. Absorption of radiation is not an instantaneous event and although the infrared is being presented to the sheet at the speed of light, the cellulose fibre is not necessarily able to absorb all the energy at this rate, hence a degree of reflection.

There are a number of factors that should be taken into consideration when manufacturing an effective reflector. The first factor concerns the materials used to provide a reflective surface and suitable substrate. By far and away the most common material used is gold. Although it is relatively expensive, it is an inherently good reflector of the wavelengths of infrared that we are concerned with, is a good conductor of heat that is not reflected and above all it is maintenance-free as it will not tarnish.

The second factor that ought to be considered is the physical shape of the reflector as the incident angle of the radiation plays a role in the rate of absorption. It is a well-documented fact that the maximum absorption by a body of infrared will occur when the radiation is presented at 90°, or normal, to the sheet surface. Lambert's cosine law quantifies the loss of absorption of radiation through reflection by determining that if the receiving surface is moved away from the normal by an angle $\theta$ the intensity of the radiation received is proportional to the cosine of the angle $\theta$ between the normal to the surface and the direction of the radiation.

If the coated sheet is relatively lightweight and there is a possibility that some of the incident radiation may be transmitted and pass through the sheet, a passive reflector is installed opposite the infrared emitter on the uncoated side of the sheet. This reflector also benefits from Compact's cold gold and the orientation of the reflector plates ensures that the radiation stays within the confines of the dryer where it will contribute to the heating phase of the drying cycle. Infrared radiation lost from the confines of the dryer and scattered around the mill is a waste of energy and should be minimised.

The lamps and gold reflectors have to be protected from the dirty environment found around coating stations and to achieve this, the Titan uses Quartz Protection Tubes (QPT). The QPT is a collection of hydroxyl-free quartz tubes that are installed so that they form a continuous sheet of quartz across the front of the dryer. The fact that they are hydroxyl-free means that they are practically invisible to the wavelengths of infrared that the lamps emit and so they absorb very little infrared. This is beneficial as it means that useful radiation is not being filtered out of the system, and also means that the front of the dryer does not run too hot, so will not pose a fire risk. In fact, the dryer face cools to touch within 2 seconds.

There are two benefits of using QPT as a method of protecting the internal workings of the dryer. Firstly, they are very cost effective and secondly, they are strong yet use less material than a plate. This means that there is less quartz to absorb the infrared from the lamps and this helps keep the face temperature down.

Applying heat to the sheet and the coating is not drying it is merely heating. Evaporation is a cooling process and evaporation is the mass transfer of water vapour from the sheet and or the coating. To achieve commercially acceptable levels of mass transfer, the water vapour in the coating needs to be given some encouragement that extends beyond the application of heat.

The boundary layer must also be considered. The boundary layer is a lubricating strip of air between the moving sheet and the relatively static surrounding air. At the interface between the sheet and the air the boundary layer has a velocity that is virtually the same as the sheet, so the air in the boundary layer appears stationary relative the sheet. This means that as the water vapour moves from the coating to evaporate it encounters a stagnant air mass, which becomes saturated quickly.

For effective evaporation to take place, a vapour pressure differential needs to exist between the area where the water vapour is and where you want it to go, with a higher vapour pressure existing where the water vapour needs to be removed from. When the boundary layer becomes saturated, the vapour pressure differential between the coating and the surrounding air reaches equilibrium and evaporation stops and the sheet and coating heat up.

The Titan dryers benefit from active boundary layer management facilities that scrub the boundary layer from the sheet surface as the sheet enters the dryer and replace it with a dry air stream of low relative humidity. This creates room for the water vapour liberated from the coating to move to as the coating is heated. At the exit to the dryer the now saturated boundary layer is removed from the sheet surface and again replaced with a low humidity air stream that allows evaporation to continue in the machine direction.

The air used for the mass transfer is used to cool the internal workings of the dryer so the heat picked-up by the air as it passes over the hot components in the dryer is not wasted but used to great effect in maximising the mass of water removed per kilowatt consumed.

Irradiating the sheet with infrared and heating the coating from the sheet-coating interface while keeping the coated surface cool by ensuring the perpetual removal of water from the coating not only saves money due to being an efficient way of removing water, but it serves to deliver excellent quality in the finished product too.

The length of the dryer in the machine direction and the use of the active airflow to remove the water vapour mean that the majority of the water required to be evaporated in order to immobilise the coating is done in a single pass. This strategy keeps the water vapour on the move and delivers a high degree of control over the potential migration of the binders in the coating.

If the coating is allowed to overheat and the surface of the coating becomes sealed due to the temperature induced cross-linking of the latexes in the coating then the water remaining in the coating will seek refuge in the sheet structure. When this happens, some of the binders that hold the coating in-situ on the sheet surface are taken with the water. This results in the appearance of mottle and more importantly dusting from the sheet surface, which plays havoc with effective lay down of ink during the printing process. A booked sale returned from a customer is very expensive recovered fibre indeed!

The Titan's active air management system and the fact that the coating is dried from the base up, with a high vapour pressure being created in the substrate means that the water vapour is encouraged to flow from the coating to the atmosphere. The high vapour pressure in the sheet structure provides a partial barrier to the uncontrolled ingress of water from the coating. The combination of high intensity heating and active air impingement provide a very useful tool in the control of binder migration.

Controlling binder migration offers some very real cost-savings. First of all there is the possibility of reducing expenditure on chemistry due to the ability to control the binders with the infrared dryer. Secondly, the output from the infrared dryers is flexible and can be run in a closed loop linked to a scanner. Changes to the required energy output are nearly instant guaranteeing minimal losses through quality issues with the drying output flexing automatically to accommodate any variation in drying requirement. Monitoring the coat dryness and using this information to drive the infrared dryers maximises the energy efficiency as well as quality control.

As discussed earlier, one of the most pressing issues of the day is the rational use of energy. Saving energy has some environmental benefit, but on the whole, shareholders care more about enhanced shareholder value and saving energy pays dividends, literally.

As an example of the potential benefits we will look at the installation of Compact Engineering's Titan infrared dryers at the Äänekoski paper mill belonging to m-real.

## m-real Äänekoski Paper Mill

The off machine coater at Äänekoski is 3900mm wide and runs at speeds of between 720m/min and 1100m/min on grades of between 115gsm and 300gsm. The original infrared dryers were manufactured by IRT and were installed with the coater at the end of the 1980's. The off-machine coater has two coating heads and the sheet run is the same through each coater. Prior to the re-build, the sheet left the coater vertically and ran through two frames of infrared with reflectors on the uncoated side of the sheet and into a hot air dryer with a length of approximately 1800mm. The sheet then turned around a roll and went through a second hot air dryer with a length of approximately 3000mm and then round another turn roll and through a second set of infrared dryers and reflectors before going through a third hot air dryer, MD length 1800mm. The sheet then went around another roll towards the next coating station as seen in *Figure 3*.

The re-build involved the renovation of the first and third hot air dryers and the result of the re-build was an increase in their moisture removal capability by the order of 30%, the middle hot air dryer was left untouched. The re-build also entailed the removal of the infrared drying frames and associated reflectors immediately after the coater and the removal of the two infrared dryers and reflectors that were installed after the second hot air dryer.

The Titan dryer frame and associated reflector were installed immediately after the coater where the first two infrared frames were previously located.

The layout for the second coating station is very similar to the first and the rebuild followed similar lines.

In this example the Titan dryers have been installed specifically as heaters to provide all of the sensible heat input to raise the coating temperature to the constant rate temperature before the sheet enters the hot air dryers.

The action of the Titan dryer appears to make the water in the coating more available to the hot air dryers than anticipated. The results below are the initial results gained by the mill immediately after the system was installed and the mill has reported better energy savings since these results were collated.

## Results following the re-build.

The installed capacity in kilowatts prior to the re-build was 1963kW per coating station. Following the re-build this was reduced to just 1300kW per coating station, a reduction of 33%.

The lightest sheet that is made on the line is 115gsm and this is produced at around 1000m/min. Prior to the replacement of the infrared, the first coating station required, on average, 507kW and the second coating station 506kW. These figures have been reduced to 323kW and 322kW a saving of 36%.

On a medium weight sheet of 150gsm, also produced at around 1000m/min. the previous average power input was 947kW and 896kW per coating station. These figures have been reduced to 729kW and 713kW an average reduction of just over 20%.

On the heavier weights, the reduction was around 30% with average energy being reduced from 1015kW on the first station to 701kW and from 970kW on the second station to 659kW while drying a 250gsm sheet at 722m/min.

The mill generates electricity locally via a combined heat and power plant and is able to buy the power at 3.5cents/kWh. There is an opportunity cost associated with this arrangement, as the power can be sold locally for twice as much if, it is not consumed by the mill.

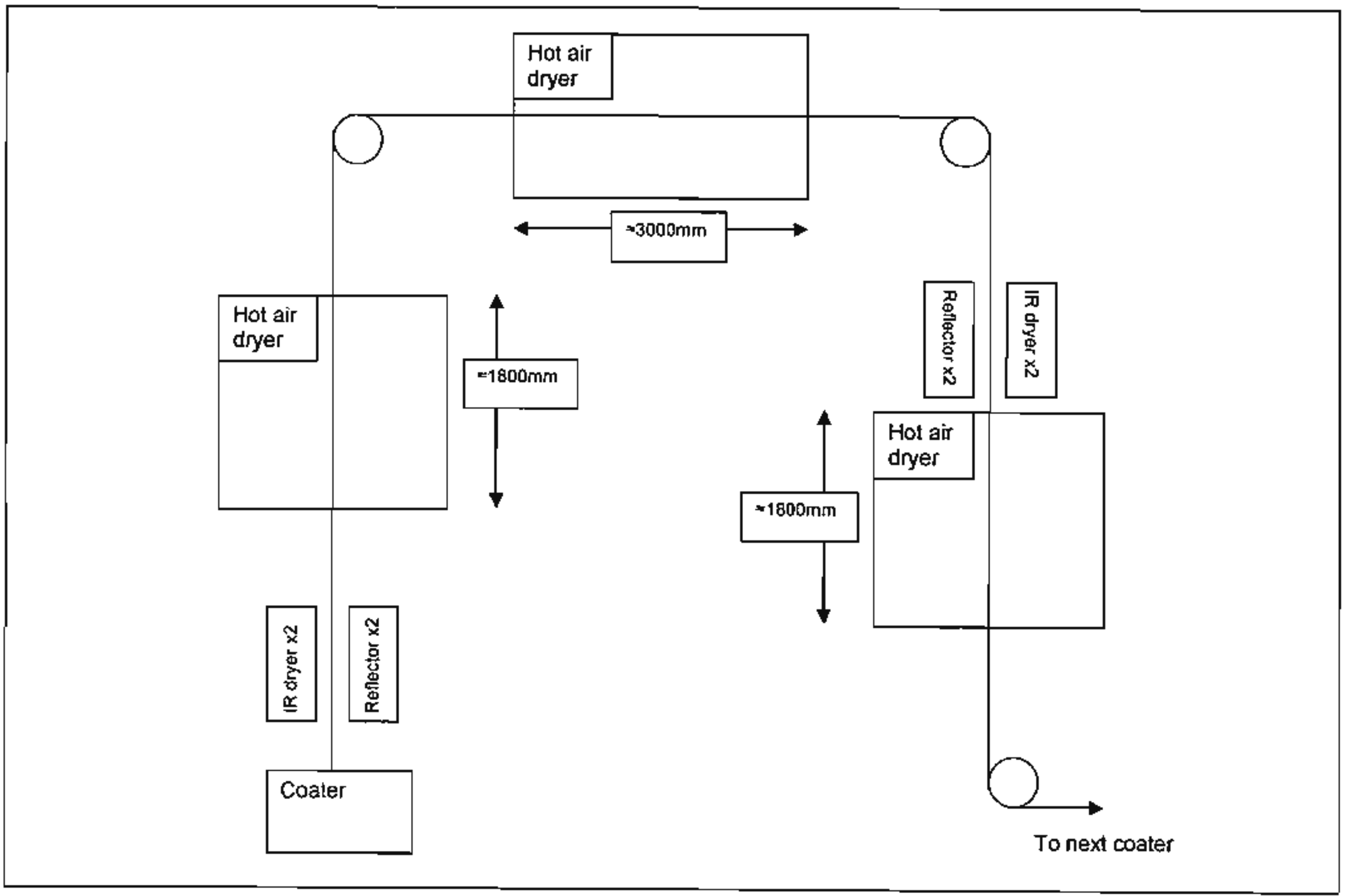

Figure 3. Diagrammatic representation of the sheet run prior to the rebuild.

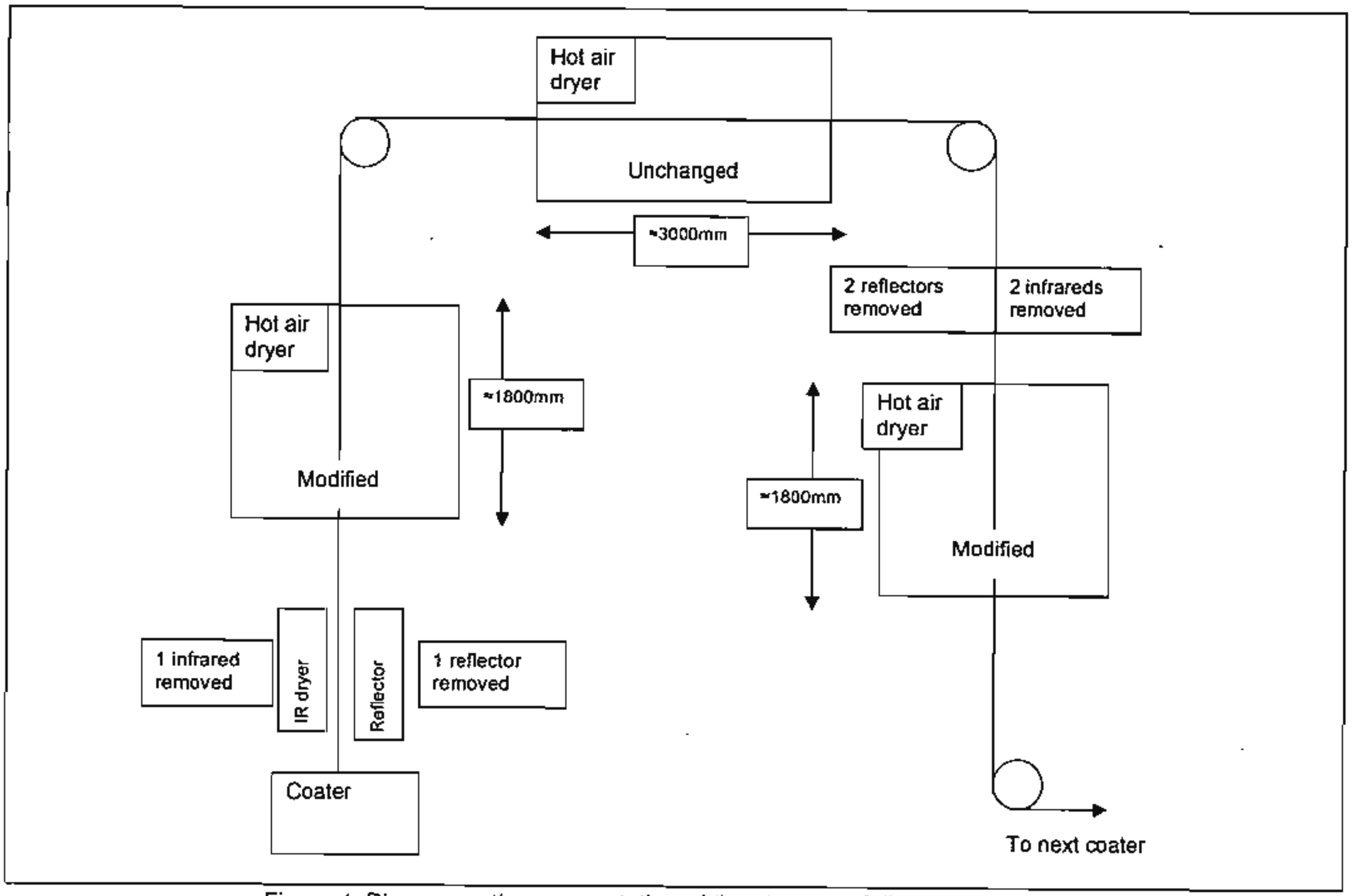

Figure 4. Diagrammatic representation of the sheet run following the rebuild.

The saving in energy can be directly translated into an additional income stream assuming that the system is running for 8000 hours per annum or 22 hours a day. The lowest energy saving is on the lightest weigh sheets and this amounts to approximately €206,000 per annum. On the heavier weight sheets the potential increases to €350,000 per annum.

The installation at m-real Äänekoski utilised much of the existing equipment from the previous infrared dryer installation and so represented a low-cost method of cost reduction. The payback period on the invested capital, using the cost savings as the only means of amortising the capital expenditure and using the initial results as the performance criteria, is around 300 days. In light of recent anecdotal evidence from the mill, the new performance levels are better and these would reduce the payback time to nearer 210 days.

The mill is still experimenting with the Titan dryers and optimising the balance between the use of the infrared dryers and the after dryers and as a result the total energy being consumed by the infrared is falling.

## Conclusion.

It represents a great leap of faith by the mill to have invested in a technology that shows such a reduction in energy requirement. In reducing the power available to be applied to the sheet Compact were essentially removing any contingency plan that the mill may have wanted, should the projected improvements not have materialised.

However, the success of the project only goes to show that those mills that are prepared to take a perceived risk and make an investment in the most modern technology will be the same mills that are rewarded with superior returns on invested capital.

There is no immunity from risk for any corporation and failure to embrace managed risk in the form of investing in new technologies only exposes companies to the far greater yet unappreciated risk of doing nothing.

Saving energy should be an obvious target for most mills as it is environmentally responsible and fiscally astute. While many companies make much of their environmental credentials, it is inevitable that shareholders are most interested in enhanced shareholder value, or more prosaically, money.

Hitting both targets at once is a boon for everyone involved.

## NOTES

# Design of Coating Structure for Flexographic Printing

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SESSION TWO
PAPER SIX

## Abstract

In flexo printing, advances in plate making technology and pre-press have improved the quality greatly and allow flexo printing to compete effectively with rotogravure and offset quality. Substrate requirements include the correct surface topography and porosity to enable good transfer of the ink to the surface. The surface energy of the substrate may need to be altered to ensure good wetting of the ink, with no reticulation.

This study investigates the influence of different pigment types, binder levels and calendering conditions on the structure of board coatings. Specifically the influence of calendering conditions on topography, surface porosity and absorbency are considered. The board samples were then printed using a laboratory flexo printer and the print characteristics studied.

Selected samples were submitted for sectioning using a Focussed Ion Beam (FIB). This enabled the penetration of the ink into the coating layers to be visualised.

## Introduction

Flexographic printing is an expanding printing technology, its growth being partly linked to its increasing use for printing packaging materials in combination with its much improved print quality and versatility. The main areas of growth have included pre-printed corrugated board(1).

In Europe, the flexography market share was 45% in 1990 increasing to 50% in 1995 and was forecast at 55% for the year 2000(2). It is now the dominating process in packaging. Over 90% of the post-print corrugated market is held by flexo and 95% of the pre-print market(3).

Trends in packaging include the increasing number of colours used(4), and also an increasing share of printing carried out by UV curing flexo inks(5). The growth of the UV market is largely attributed to environmental reasons(6,7,8,9) but its versatility and ability to print on almost any substrate are probably also drivers for its growth(10). There are some documented problems such as slight odour, lower colour intensity, gloss and abrasion resistance(7). There is a strong trend towards 'point-of-sale' printed products, especially in the linerboard sector(11,12,13).

The key developments in the flexo printability, have occurred from the 1970's to current day, include computerisation of almost all press functions, improvements in narrow and mid-web sleeve technology (1990's), gearless direct drive technology and new plate making systems (1990-2000). A modern flexo press may print up to 12 colours simultaneously at a resolution of 175 lines per inch and at a printing speed of up to 600 m/min(11).

Flexography is a versatile process which is used to print a wide variety of substrates, making it more difficult to summarise concisely the requirements of the substrate for good print runnability and quality. Both surface energy and topographical aspects of the substrate are discussed in the literature. Aspler *et al* studied the surface chemistry of different surface sized linerboards using inks with different polarites. They showed that surface chemistry of the board was a less important feature than its formation and topography for obtaining good print quality. The polarity of the ink however had a significant influence on its rate of penetration. When a commercial ink with a low polarity and surface tension was used, the surface sizing acted purely as a mechanical barrier to ink penetration. However when a high polarity and high surface tension ink was used, the paper surface size had a considerable influence, preventing transfer of the ink and low print density.

However in work by Mesic *et al*(16) there was little difference observed between the print quality observed from printing with surfactant modified ink, or ones which had no surfactant treatment. In this work it was shown that Corona treatment of the substrate improved both the print quality (spreading rate of the ink on the surface was faster giving better full tone printing) and also the ink rub resistance. The topography of the surface was also shown to be an important parameter in obtaining a homogeneous ink film layer and less mottle and unprinted areas. Rentzhog(18) studied the influence of water based flexo ink parameters on the print quality of printed PE coated board. She found that ink transfer correlated well with the ink plastic viscosity and surface tension, and that the most transfer was achieved at intermediate values of these. Print mottle was mainly caused by 'dewetting' of the ink, which then forms rivulets on the board surface. Print mottle was decreased by increasing the solution polymer content of the ink, which served to increase the low shear viscosity and decreased the surface tension.

Methods to evaluate topography and its relationship to flexo print quality were comprehensively discussed by Barros(17). He used an optical imaging technique 'OptiTopoTM' to determine the topography of the linerboard and its relationship to the print quality. He determined the size of surface depressions in the substrate which led to bridging of the ink across the substrate leading to local uncovered areas. These were visually observed as white areas and were detrimental to the visual appearance of the print. Good recent reviews of the flexographic process are included in Rentzhog 2006 and Barros 2006(17).

In this study, a number of different pigments have been used to coat a white top board using a range of latex levels. The coated boards were then finished using two different calendering regimes. The aim of the work was to study the influence of these different parameters on the surface porosity of the coating and the printability. Measurements of printed dot area, print density and Focussed Ion Beam (FIB) determination of ink penetration were used to determine the distribution of the ink in the printed state.

## Experimental

### Materials

Four carbonates were selected which varied in their particle size distributions, and were coated at a range of binder levels onto a white top board using a HelicoaterTM blade coater with a pond head and stiff blade. The coatings were made at their maximum runnable solids content.

The pigments used are detailed in *Table 1*. These pigments were combined with Dow 920 latex at a range of levels (9, 12, 15 and 18 pph).

As a second part to the exercise, blends of the PCC and 3 clays were also made at a ratio of 80:20 PCC:clay at a latex content of 12 pph. The properties of the white top liner board are given in *Table 2*.

The boards were tested in their uncalendered state and using two different calendering temperatures (80°C and 140°C), using a soft compact calender (EP-210 laboratory calender from Enfoplan OY, Finland) at 40 m/min and 1 nip.

The pressures were selected to give 50 gloss with the ultra-fine GCC coating containing 12 pph latex (50 kN/m at 80°C and 25 kN/m at 140°C).

### Paper testing

An DataColor Elrepho 3300 was used to measure the optical characteristics of the papers both using D65 illumination, with and without a 400 nm UV filter. Paper brightness, whiteness and L,a,b were measured. A Parker Print Surf was used to measure roughness at a pressure of 1000 kPa. TAPPI 75° gloss was measured using a Hunter glossmeter. A Gretag densitometer was used to measure the print densities. The absorbency of the coatings were measured using a stain length test on the IGT printer apparatus. A controlled volume (~6µl) drop of Dibutylphthalate, with Sudan red IV dye was applied from the syringe to this disk, and then transferred to the sample through a nip on the IGT press at a speed of 0.5 m/s. The length of the stain gave an indication the porosity of the coating.

### Imaging reflectometry

The Imaging Reflectometer is a new instrument for quantitative analysis of surface optical reflectance and appearance. The instrument uses imaging technology to map the 2D angular distribution of light forward scattered from surfaces in the range ± 10° about an angle of incidence of 75°. The measurement geometry is applicable to most coated papers. Various features of the distribution of scattered light may be calculated (most commonly the distribution width which is a characteristic of surface waviness). The technology was originally described in papers by Gate & Leaity(20) and Gate & Parsons(21). More recent work using the Imaging Reflectometer has been reported by Elton & Preston(22), and Preston & Gate(23).

The reflectometer uses polarised light at two wavelengths to determine other surface properties, principally refractive index (a sensitive measure of surface composition) and optical roughness(24,25) (roughness features ≤ wavelength of light).

| | |
|---|---|
| Ash (%) | 4.2 |
| B'ness (D65 with –400 nm UV filter) | 74.3 |
| Y'ness (D65 with –400 nm UV filter) | 2.1 |
| L* (D65 with –400 nm UV filter) | 89.5 |
| a* (D65 with –400 nm UV filter) | –0.36 |
| b* (D65 with –400 nm UV filter) | 1.21 |
| | |
| B'ness (D65 +UV) | 74.5 |
| Y'ness (D65 +UV) | 2.3 |
| L* (D65 +UV) | 89.6 |
| a* (D65 +UV) | –0.35 |
| b* (D65 +UV) | 1.3 |
| CIE Whiteness (D65 +UV) | 69.3 |
| PPS (O/S) 1000 kPa / µm | 8.23 |
| PPS (I/S) 1000 kPa / µm | 5.2 |
| Density (g/cm³) | 0.843 |
| Caliper (µm) | 166 |

Table 2. Basepaper properties

| Pigment | Pigment Brightness D65 | Sedigraph Mass <1µm content (%) | Sedigraph Mass <0.25µm content (%) |
|---|---|---|---|
| Ultra fine GCC | 92.9 | 87 | 33 |
| Fine GCC | 93.8 | 77 | 27 |
| Narrow PSD GCC | 95.3 | 86 | 19 |
| PCC | 96.7 | 94 | 11 |
| Platey kaolin | 87.5 | 74 | 24 |
| Fine platey kaolin | 88.4 | 88 | 45 |
| Fine blocky kaolin | 88.8 | 99 | 72 |

Table 1. Pigment properties

It has been shown previously that the RI value measured by the reflectometer gives an average of the RI of the components under the beam(26,27). If a surface contains a large proportion of air, this is seen as a lower RI. The technique has also been shown to be very surface sensitive, only probing the top few microns of the surface to be studied(28). The RI has often been found to correlate with the micro-roughness of the substrate, which in turn is influenced by the pigment particles in the coating layer and the finishing of the surface.

**Printing**

The print testing was carried out using a RK Flexiproof 100 print tester. The print forme was designed to have two different screen rulings (20 and 40%) and a solid 100% coverage area. The prints were made using a water based ink at a speed of 50 m/min. The test forme is divided into two portions, which are printed with two different anilox rollers (6 $cm^3/m^2$ and 5 $cm^3/m^2$).

The print gloss of the solid area was measured, and the print density was determined for the 20, 40 and 100% areas. Dot size evaluation was carried out on the halftone areas.

**Focused ion beam, FIB**

An FEI FIB201 gallium focused ion beam instrument at the University of Bristol was used for sectioning and high-resolution imaging. The instrument can produce a 30 keV gallium ion beam of between 7 nm and 300 nm in diameter using beam currents of 1 pA and 12 nA respectively. A platinum organometallic gas injector allows deposition of platinum over selected areas of the sample, which protects the top surface of the sample during ion milling. For sample sectioning, a large ion current was used initially to remove a staircase-shaped trench. A finer beam of lower current was then used to 'polish' the larger vertical face of the trench. This was done by scanning with the beam in a series of parallel tracks from the bottom to the top of the trench. The sample was then tilted to 45° and the polished face imaged using the same ion beam (at a much lower beam current to achieve high resolution). The image below shows the geometry of the FIB 'trench' and the images in the results section are taken from the rear wall of this trench, viewed from above at an angle of 45°.

## Results

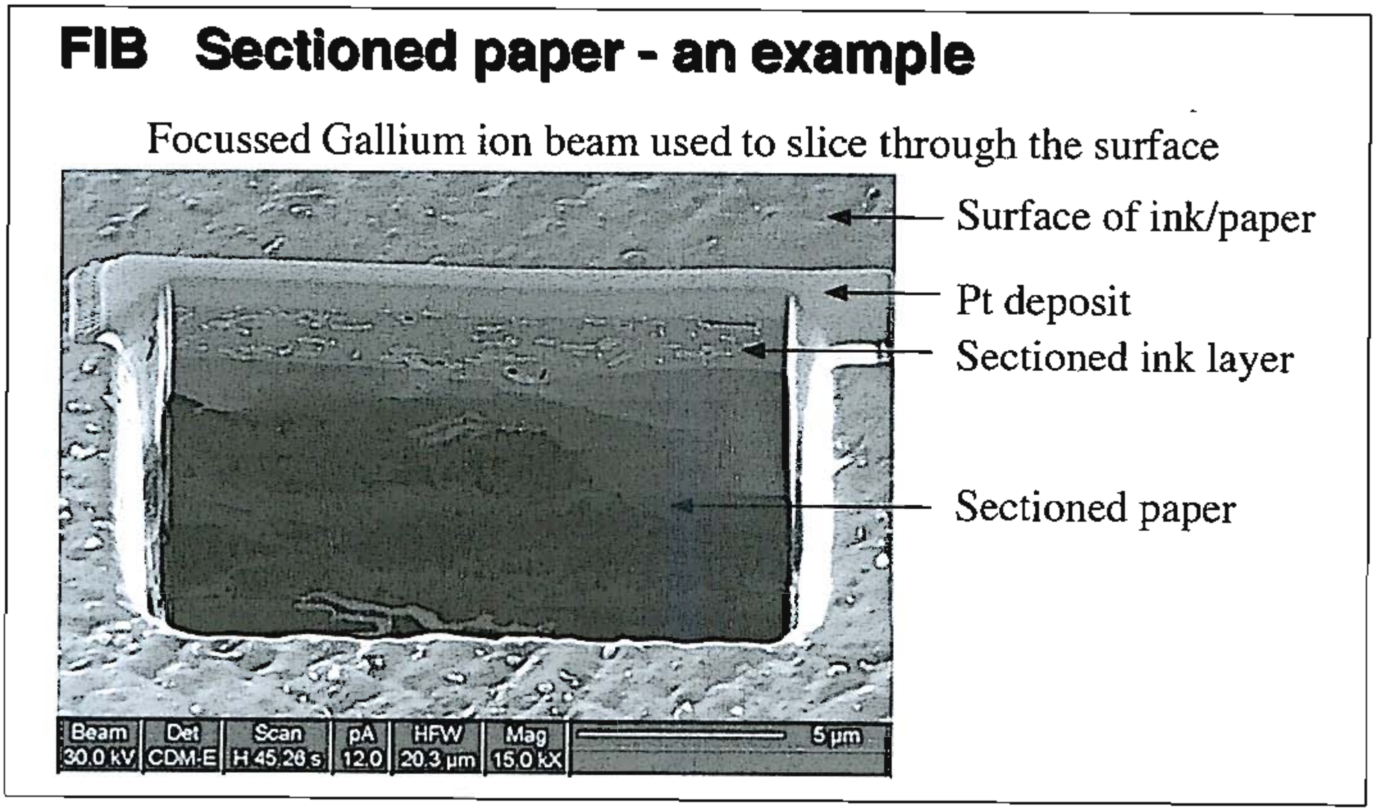
**Paper properties**

The influence of pigment type and binder level for the 140°C calendering condition on the gloss and whiteness of the paper are shown in *Figures 1 and 2*, and the brightness and PPS roughness in *Figures 3 and 4.*

The addition of latex can clearly be seen to influence the gloss of the board; a decrease in gloss with more latex occurred for every pigment. Calendering obviously raised the gloss of the surface. A very slightly higher gloss was observed for the samples which were calendered at a higher temperature and lower nip pressure. In terms of the coating pigment, the PCC coated board had the highest gloss, followed by the Narrow PSD GCC. The fine GCC coating clearly had the lowest gloss. These same rankings were observed in the brightness and whiteness measurements. Addition of more latex resulted in a decrease in the brightness and whiteness of the coatings as would be expected. However the calendering of the samples had little impact on the brightness or whiteness. The macro-roughness as measured by the PPS, increased slightly with increasing latex content.

**Imaging Reflectometry**

*Figures 5 - 8* show the reflectometry results obtained for these coatings as a function of latex level. In *Figure 5*, it can be seen that there is a large difference in effective RI of the different pigment coatings, indicating differences in the surface air content of the coatings. The PCC coating has the lowest effec-



**FIB Sectioned paper - an example**

Focussed Gallium ion beam used to slice through the surface

Example of a FIB section of a printed uncoated paper

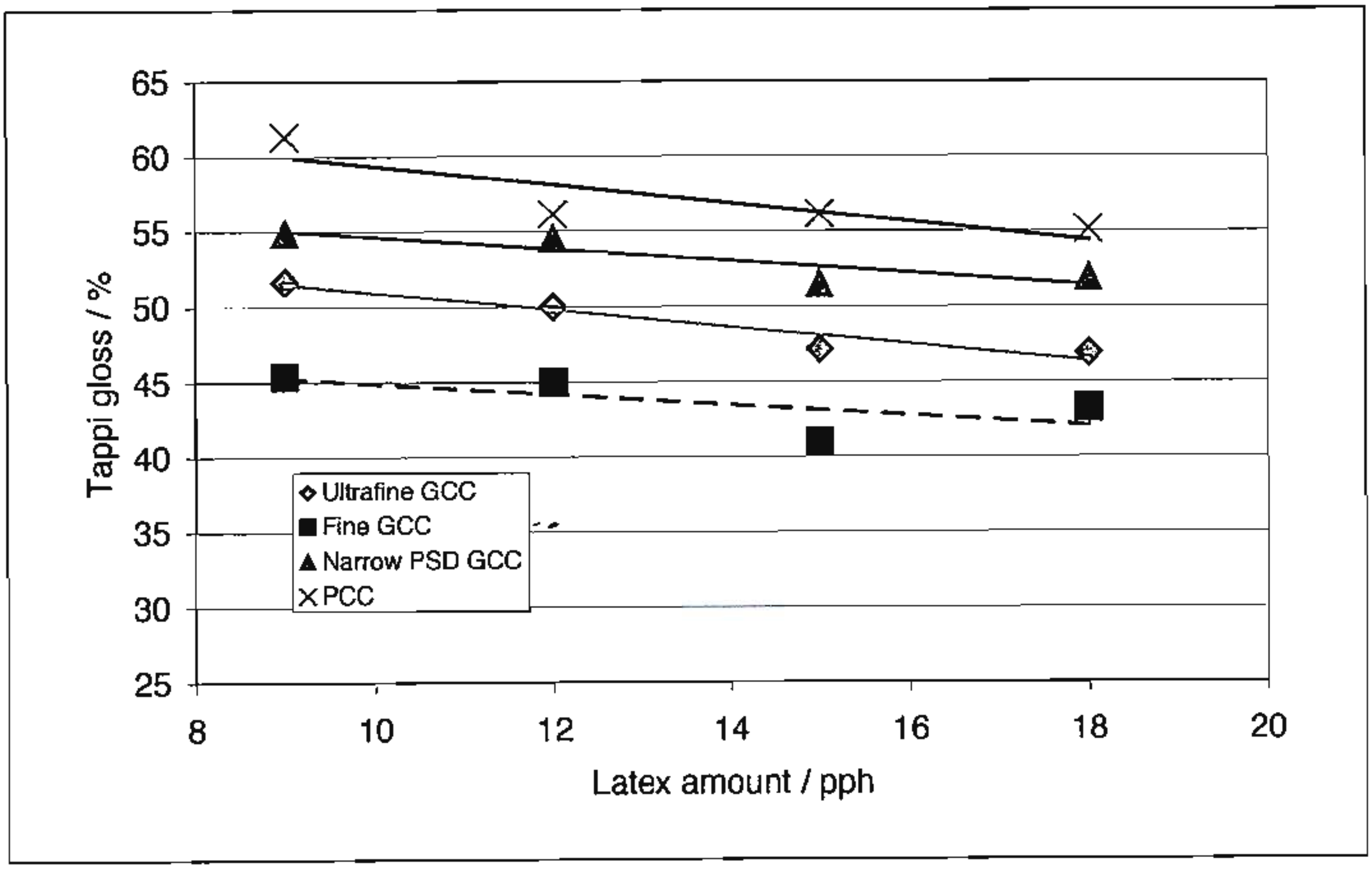


Figure 1. Tappi gloss 75° of various calcium carbonate coatings at 4 binder levels

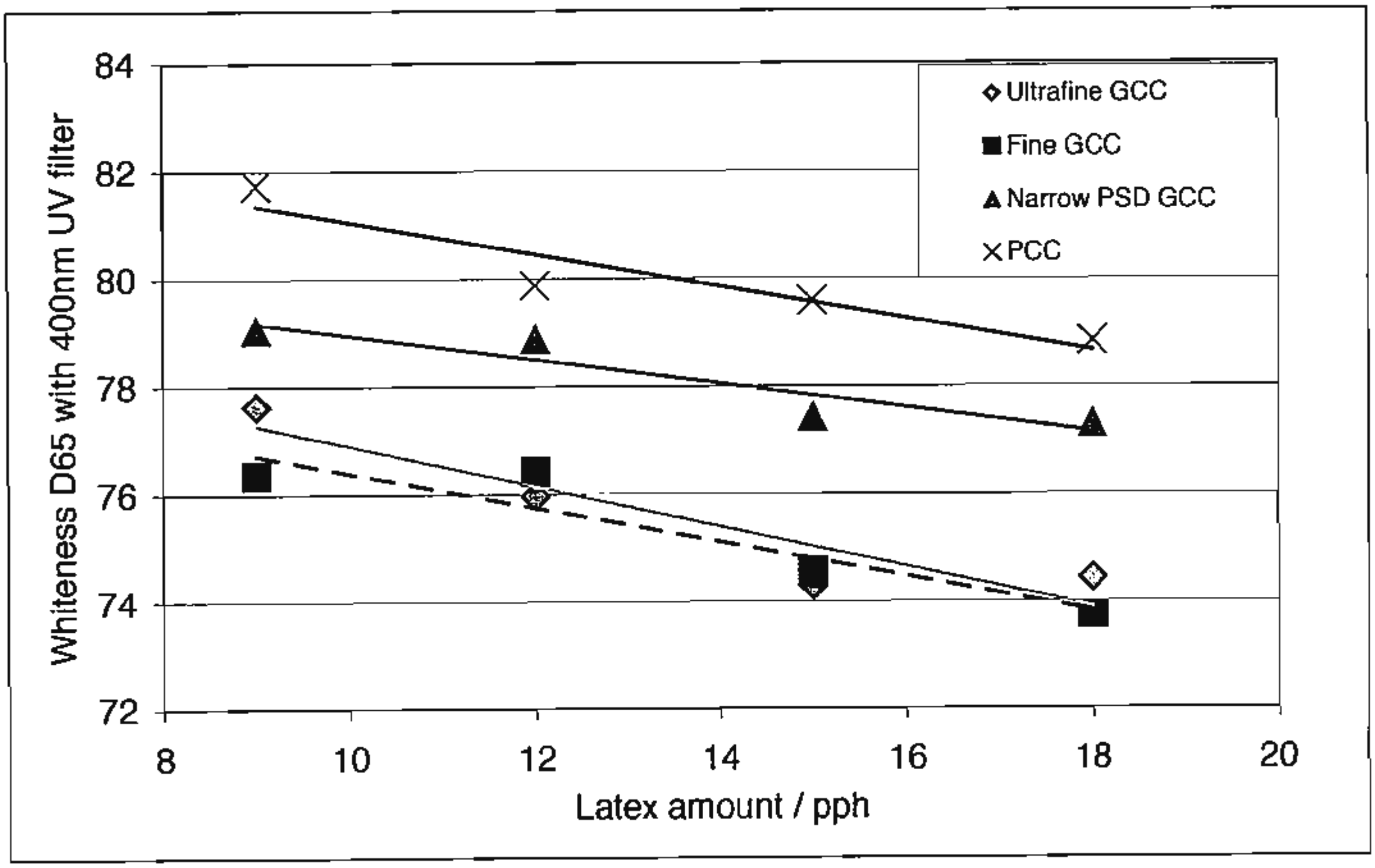


Figure 2. Whiteness (D65 with 400nm UV filter) of calcium carbonate coatings at 4 binder levels

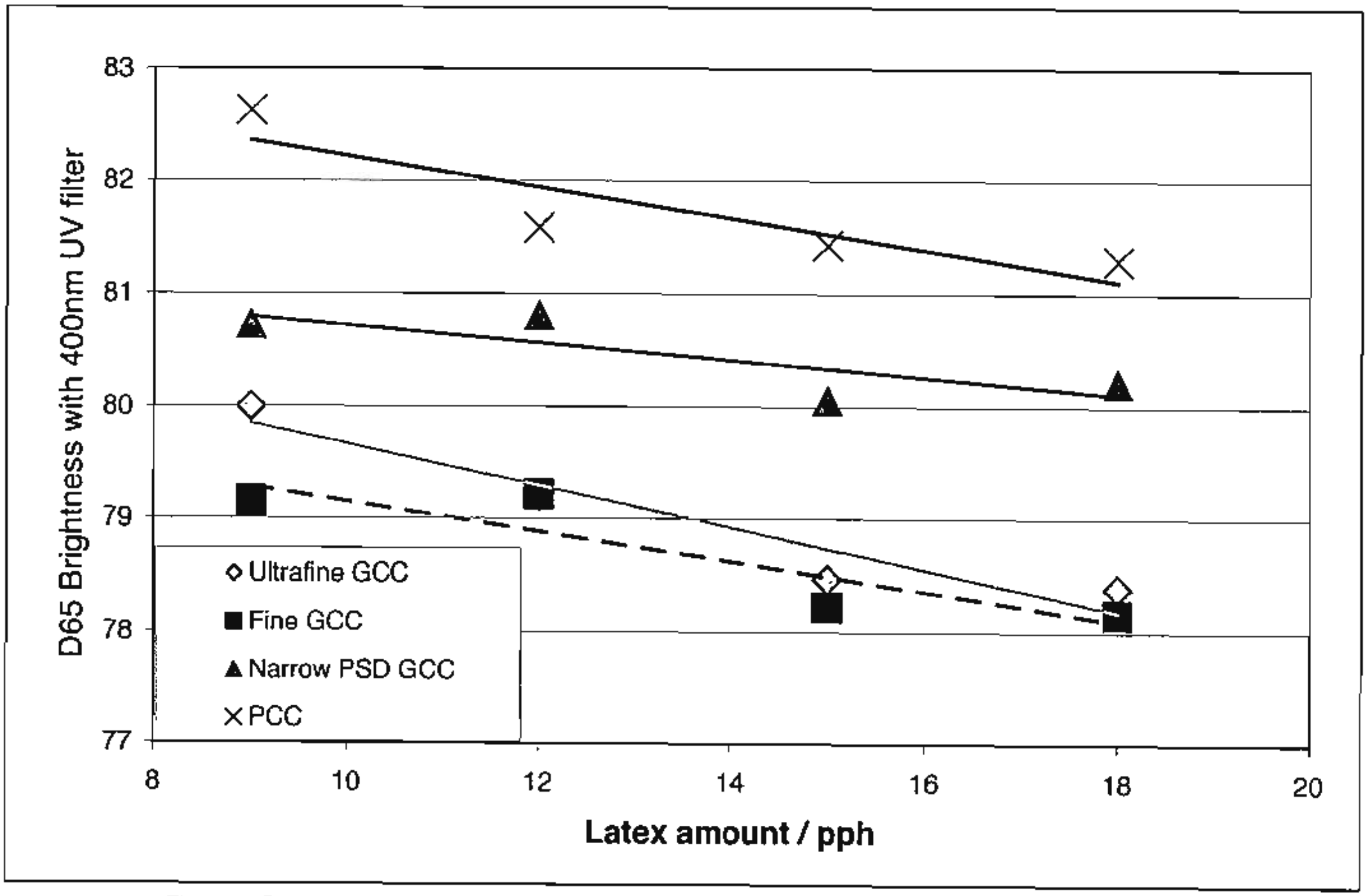


Figure 3 Brightness (D65 with 400nm UV filter) of calcium carbonate coatings at 4 binder levels

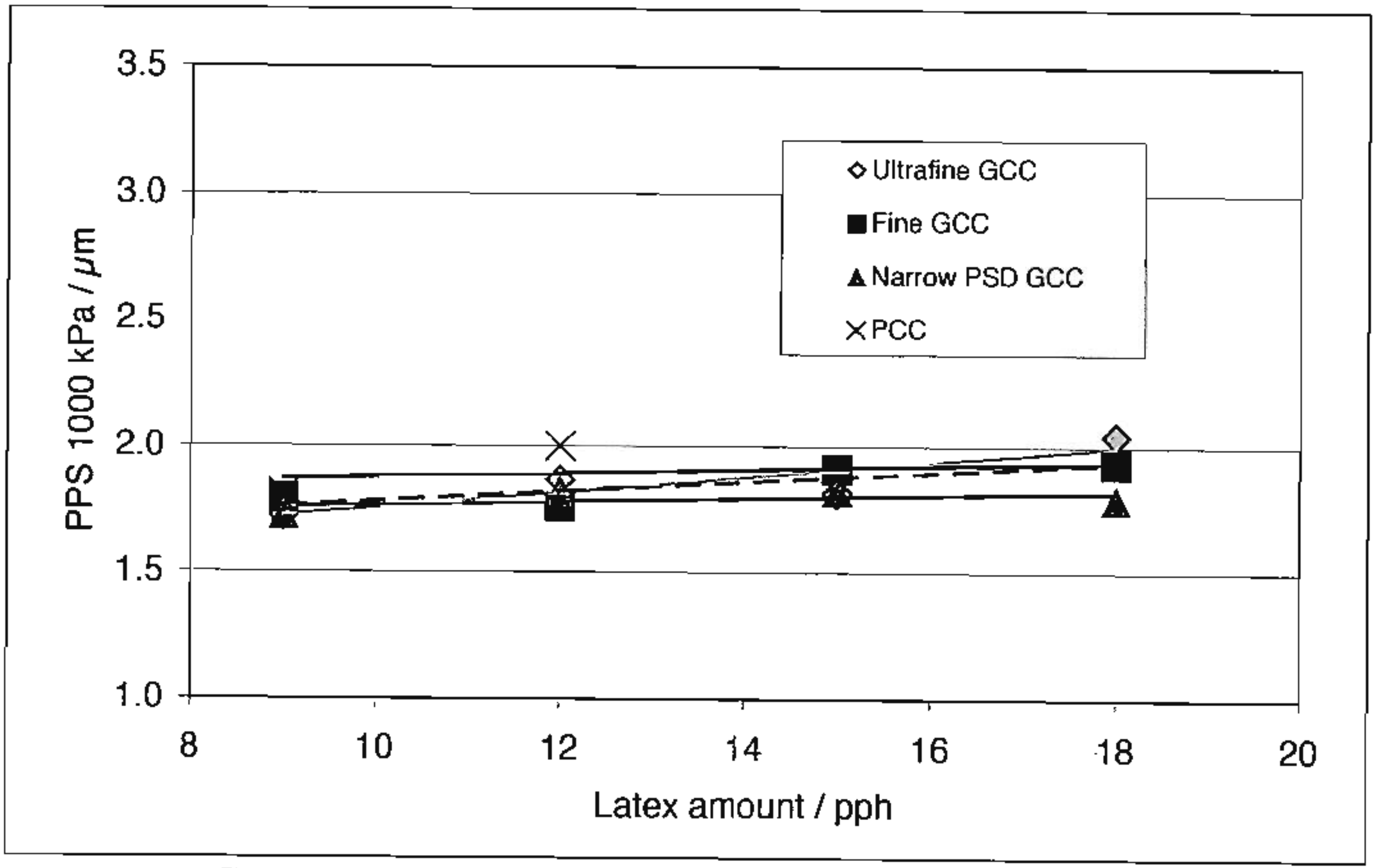


Figure 4. PPS (1000 kPa) roughness of calcium carbonate coatings at 4 binder levels

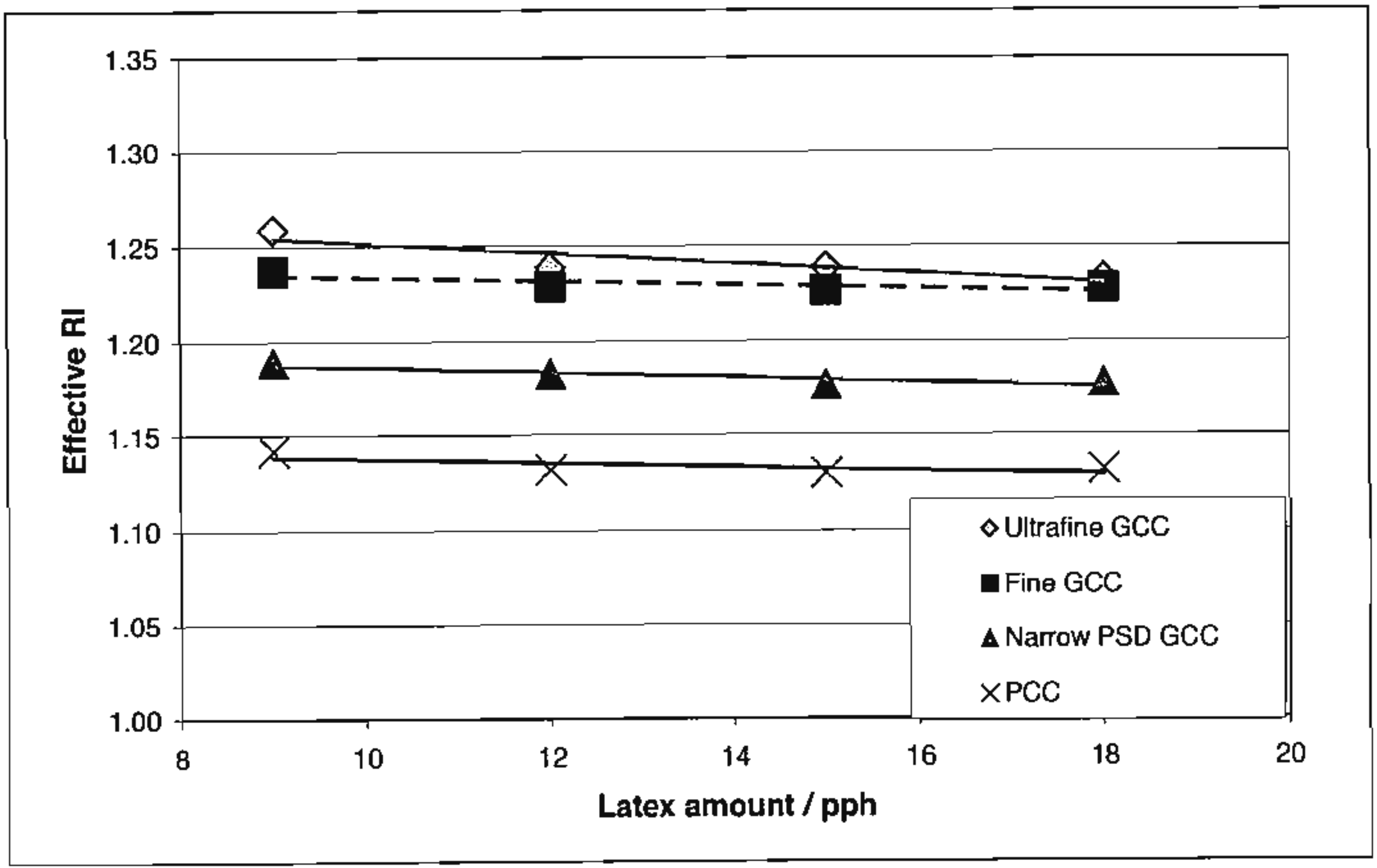


Figure 5. Effective RI of coated surfaces with varying latex level, showing large differences between different pigments, and a very slight decrease with increasing binder level.

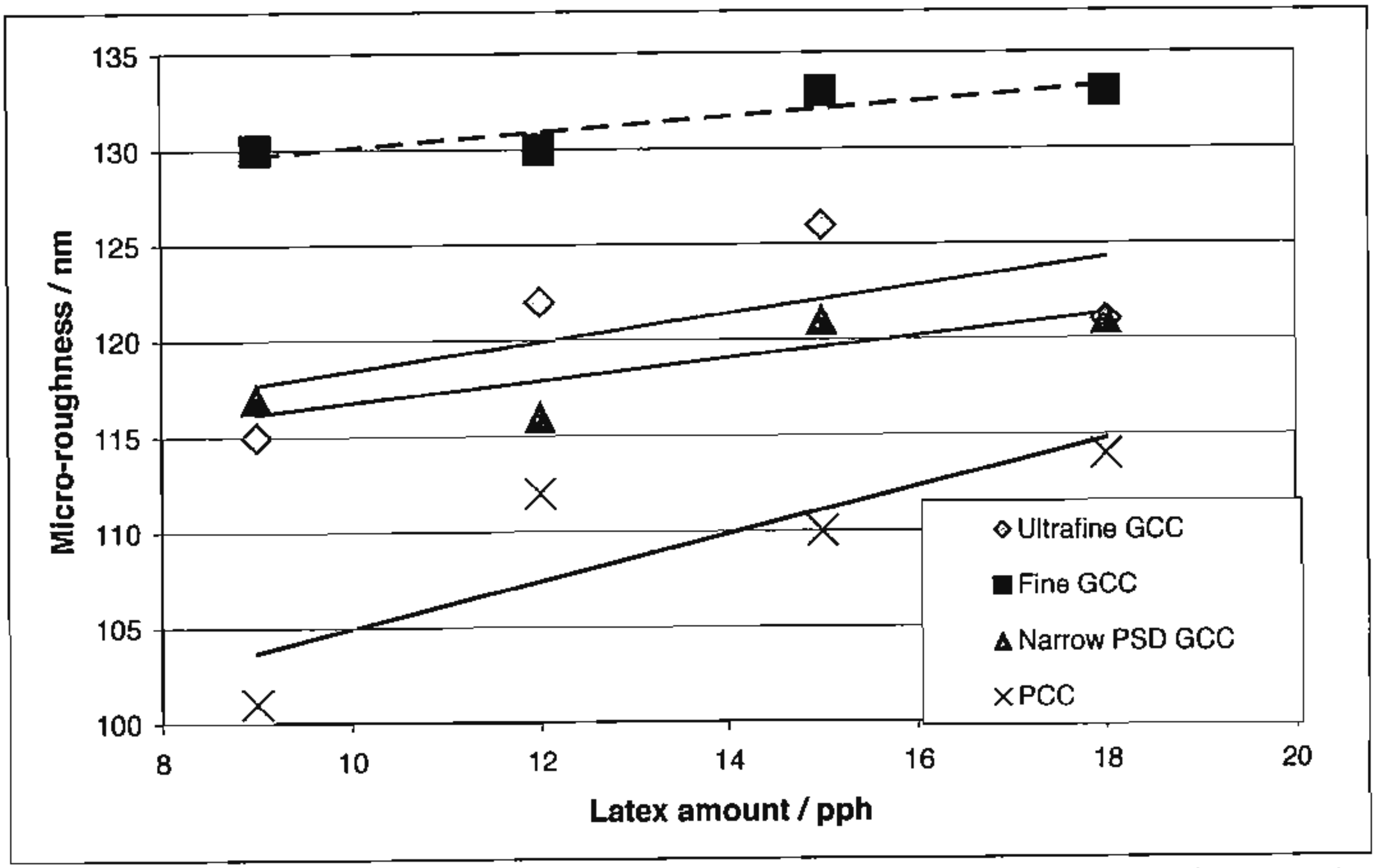


Figure 6. Reflectometer micro-roughness of coated surfaces, showing large differences between different pigments, and a slight increase with increasing binder level.

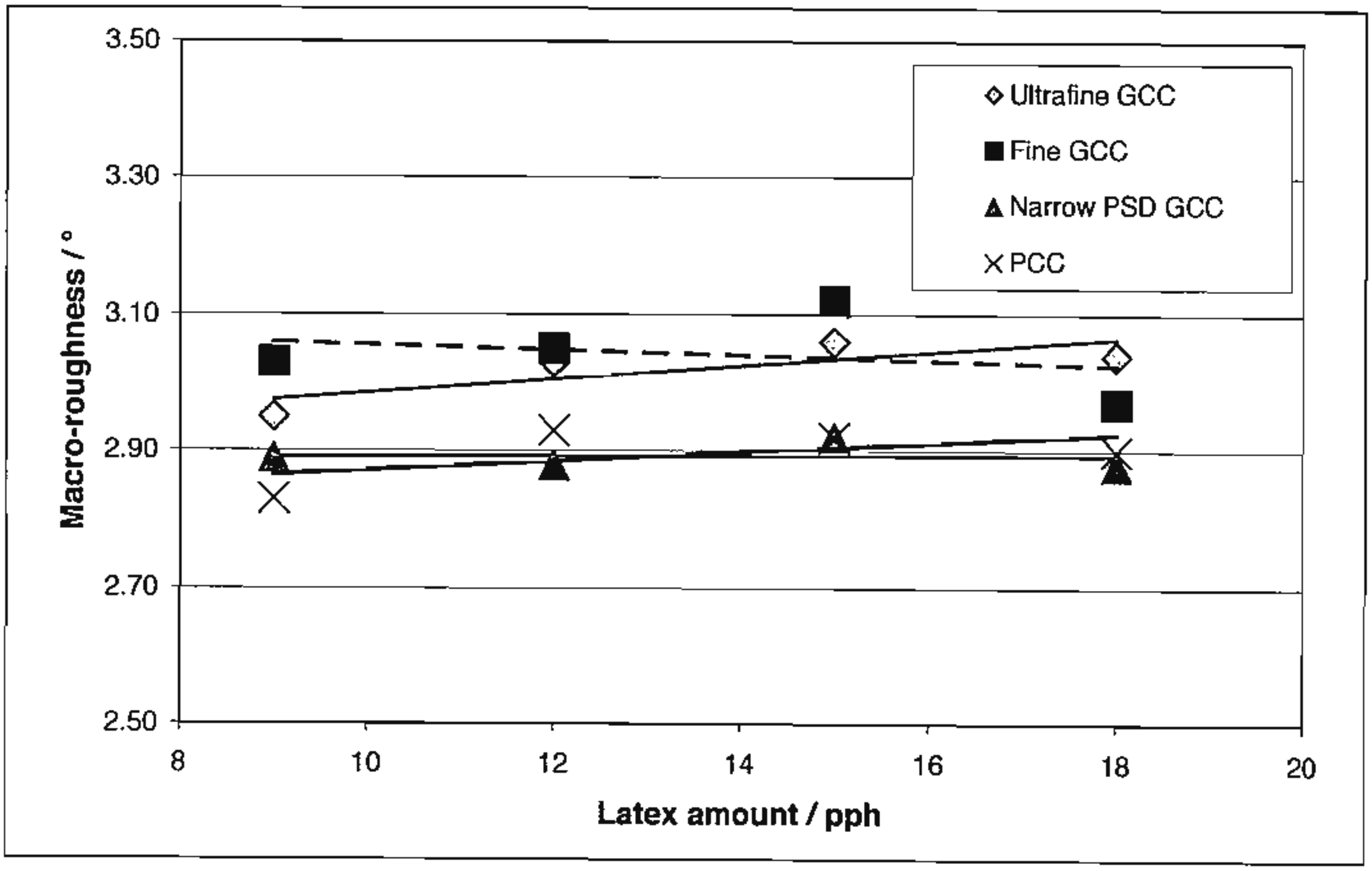


Figure 7. Reflectometer macro-roughness of coated surfaces, showing lower roughness for the narrow PSD pigments. Little change with binder content

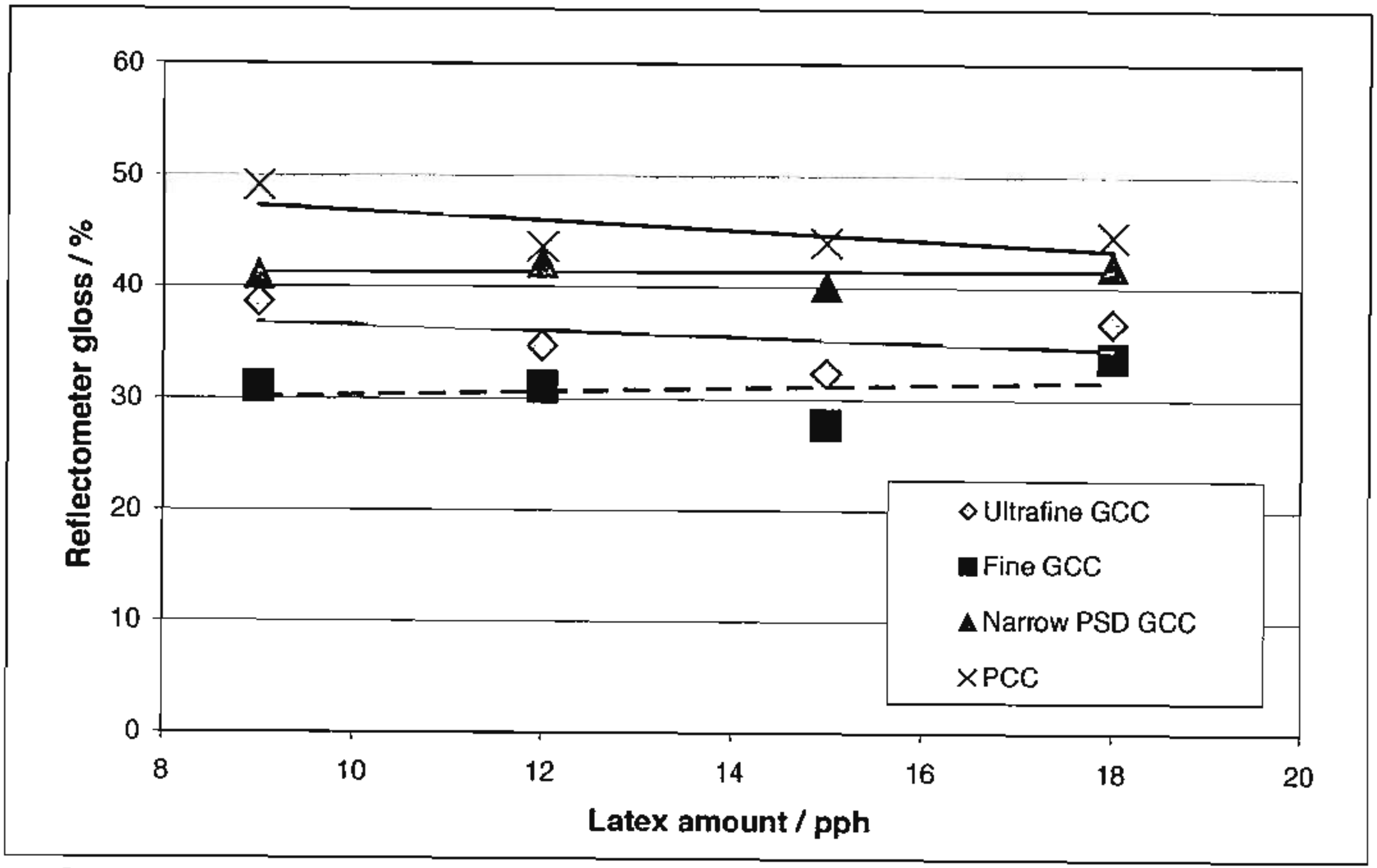


Figure 8. Reflectometer gloss of coated surfaces, showing higher gloss for the narrow PSD pigments. A very slight decrease in gloss with increasing binder content

tive RI (most porous), the narrow particle size distribution GCC coating is the second most porous coating and the two finer, broad particle size distribution calcium carbonates had the most closed surface in terms of surface air content. Calendering of the samples reduced the surface air content, probably by lowering the surface micro-roughness, compared to the uncalendered samples, but there was no real difference in the RI values for the two different calendering conditions.

Interestingly the addition of increasing amounts of latex results in a small decrease in RI. This is probably due to a slight increase in micro-roughness of the coating on the addition of more latex. The correlation between the micro-roughness and the coating refractive index is shown in *Figure 9*. However, larger differences in RI and micro-roughness are superimposed on this plot when studying the different pigment and calendering systems. This increase in the surface micro-roughness is also likely to be responsible for the decrease in gloss, as the macro-roughness is not shown to change significantly (PPS *Figure 4* and reflectometry *Figure 7*). Results such as the stain length (*Figure 10*) show that the bulk porosity of the coatings are indeed decreasing significantly on addition of latex.

The Imaging Reflectometer gloss results (*Figure 8*) show similar trends to those obtained from the Tappi glossmeter. The high gloss of the PCC coating is a result of both low micro and macro-roughness values.

### Stain length

In all cases the higher temperature and lower pressure calendering has resulted in a longer stain length, indicating a more closed surface.

The stain length for the 140°C calendering condition is shown in *Figure 10*. The trends for the two calendering conditions were very similar with respect to the pigment in the coating layer. It can clearly be seen that the PCC coating was the most porous and has the shortest stain length. The narrow particle size distribution GCC is the second most porous sample as would be expected, and the broad particle size distribution carbonates give the most closed surface. As these coatings were made onto board, it was not possible to measure the porosity using mercury intrusion porosimetry. However previous data have clearly shown that for carbonate coatings, the pore size is a function of the average size and steepness of the particle size distribution, and that the pore volume is simply a function of the steepness.

### Print Results

The samples were printed on the RK Flexiproof printer. In *Figures 11 and 12* the print gloss and delta gloss results are shown for the 140°C calendering condition. The print gloss generally increased with binder content, despite the fact that the sheet gloss decreased, so it appears that print gloss in this instance is more dependant upon ink absorption, than on the sheet gloss.

### Dot analysis

The dot perimeter gave a good measure of the ink spread and as shown in *Figure 13*, correlated reasonably well with the print density, larger dots giving a higher density as would be expected. The influence of latex level and pigment type can also be observed. As the binder is increased from 9 pph to 18 pph both the print density and dot perimeter clearly increase.

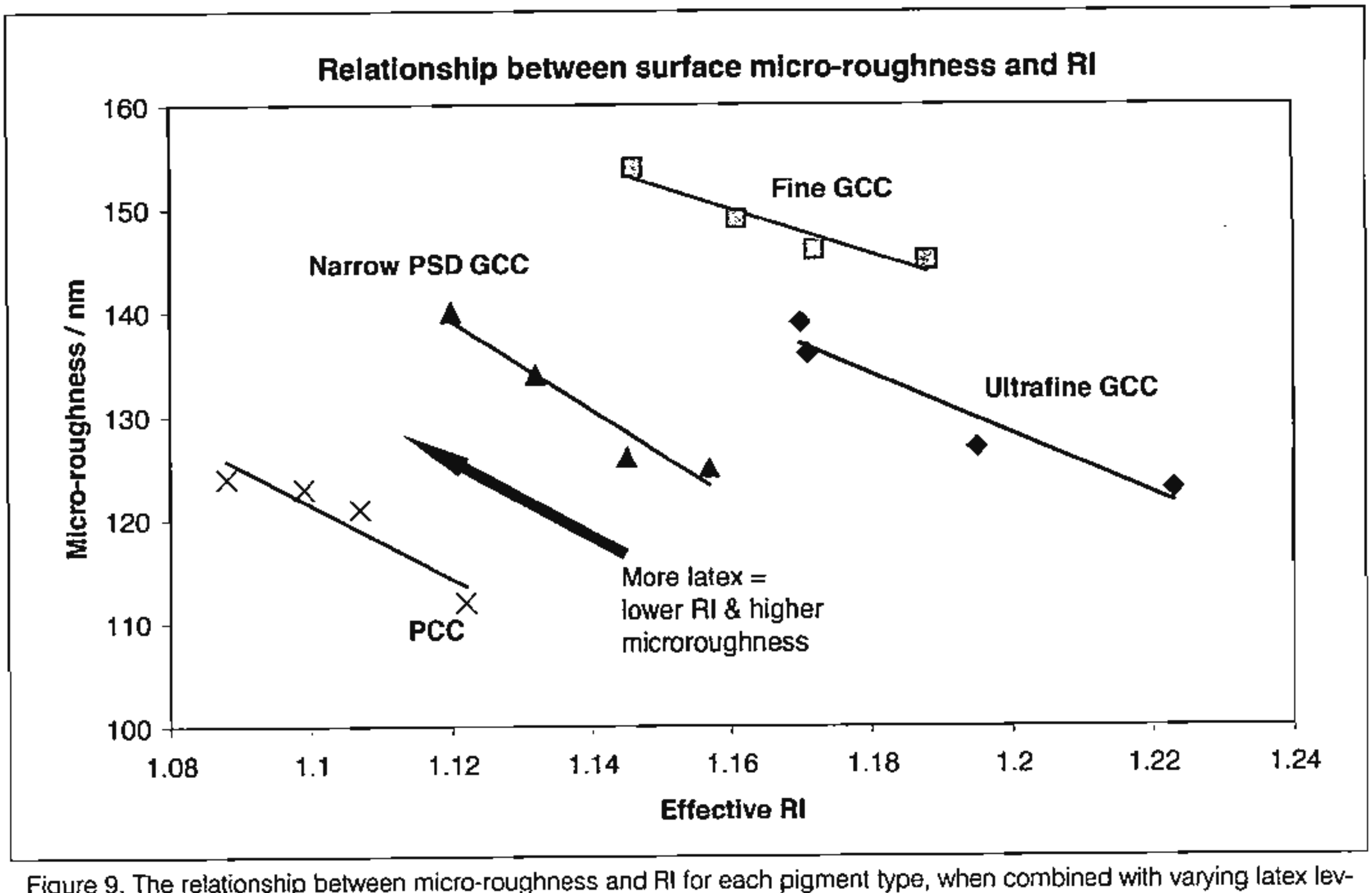


Figure 9. The relationship between micro-roughness and RI for each pigment type, when combined with varying latex levels. Increasing latex content, results in a slightly higher micro-roughness and a lower RI. Larger RI differences are seen between different pigment types.

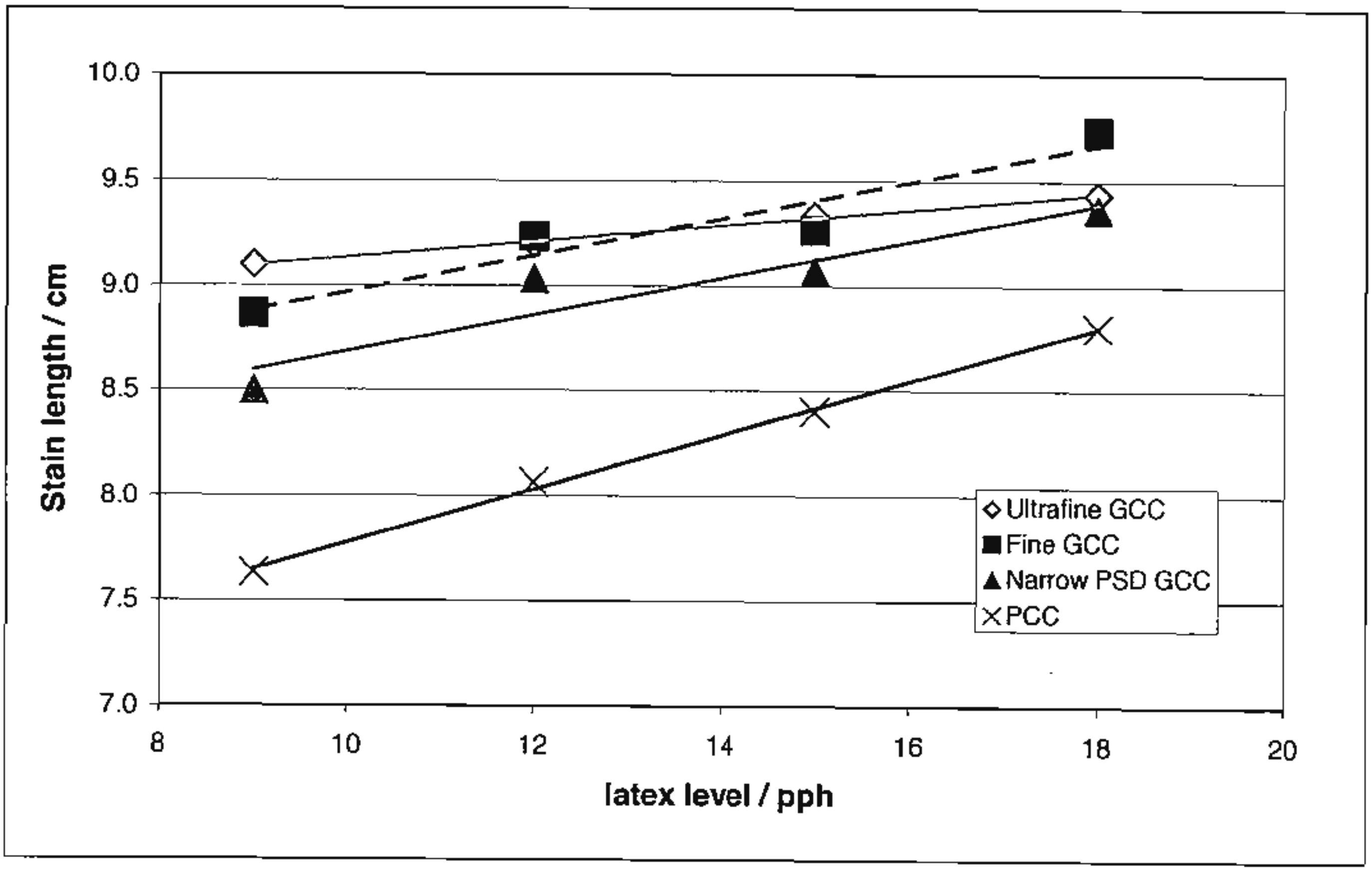


Figure 10. Stain length for 140° calendering temperature. Increasing binder, reduces bulk porosity and increases the stain length.

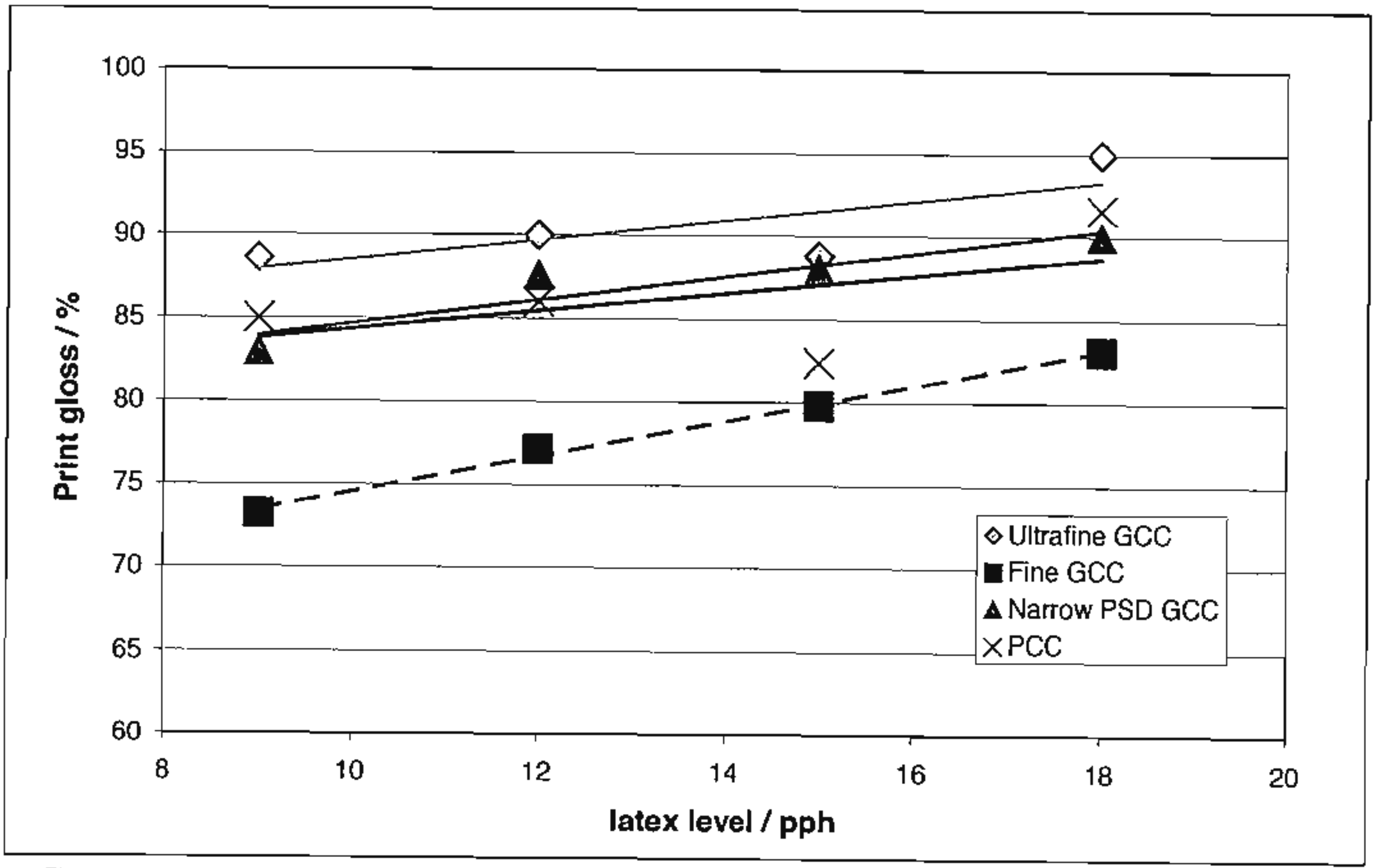


Figure 11 Print gloss of samples calendered at 140°. Increasing print gloss observed with increasing binder content - despite a slight reduction in sheet gloss, due to improved ink hold out.

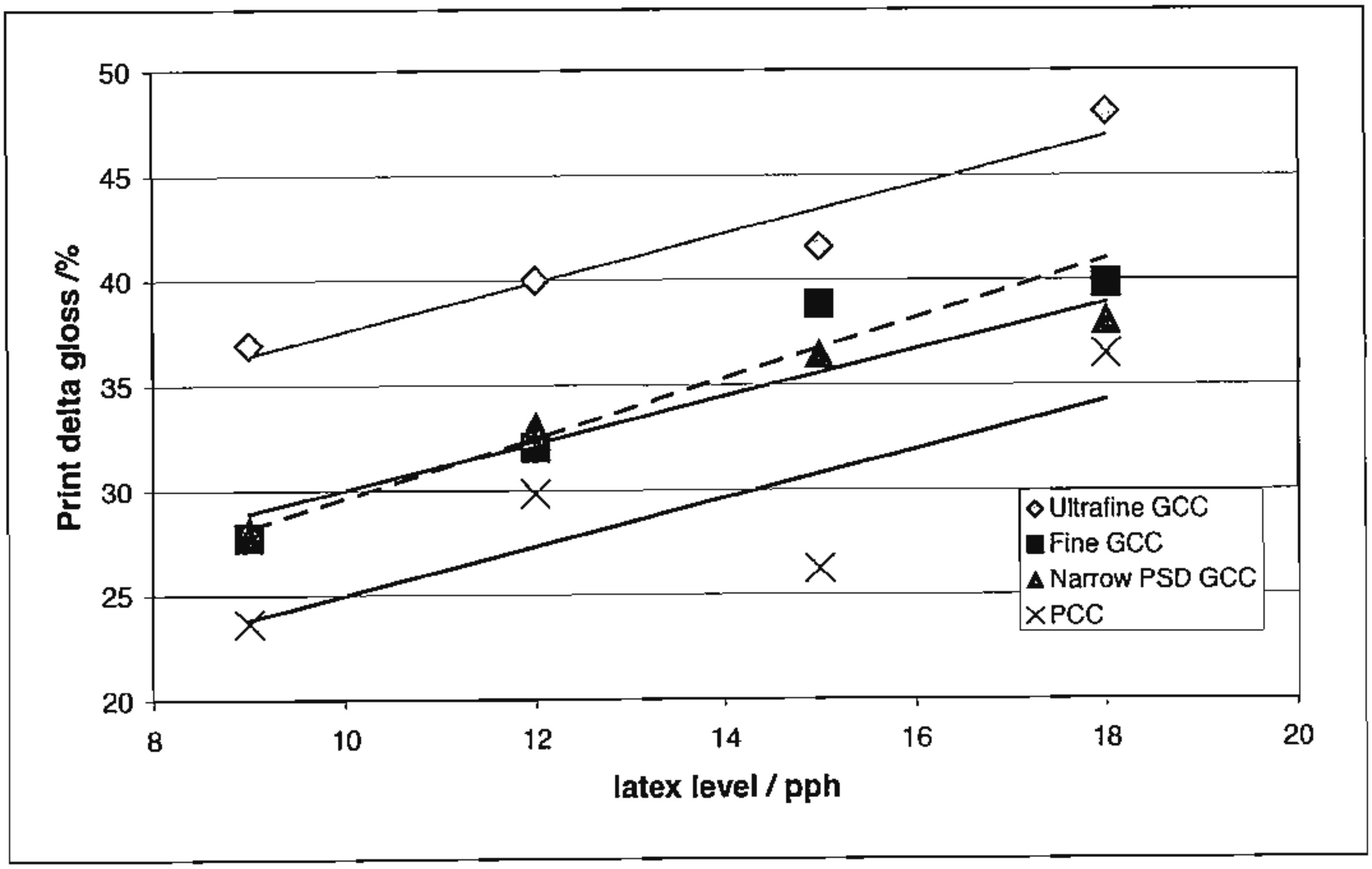


Figure 12. Print delta gloss (print gloss - paper gloss) at different latex levels

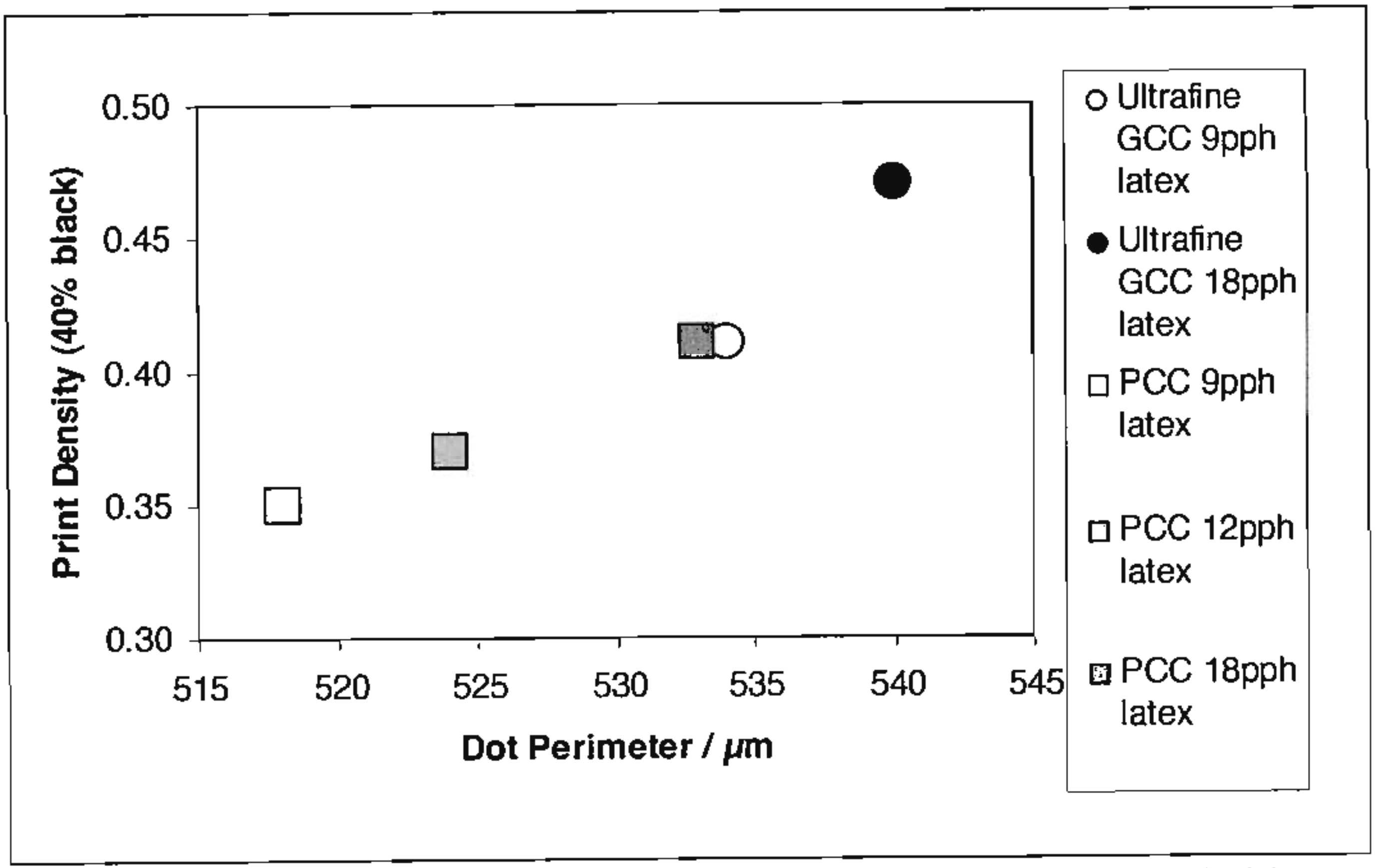


Figure 13. Black print density and dot perimeter at different binder levels (measured on the 40% black print)

This is the case for both the PCC and the Ultrafine GCC coating. The more porous PCC coating also has a lower print density and smaller dot perimeter than the Ultrafine GCC coating, when compared at the same binder level.

A summary of the printed dot results is given in *Figure 14*. The increase in binder content clearly results in a higher print density for the same ink coverage area. The pigment types fall into 2 groups, the samples which are more closed and less absorbant (Ultrafine GCC and GCC), and those which have a more porous structure and consequently a lower print density (PCC and Narrow PSD GCC).

### FIB analysis of ink penetration

Selected samples were analysed for z direction ink penetration using the technique of focussed ion beam. Sections were made through a printed dot of the printed Ultrafine GCC and PCC coatings which contained 9 pph latex. In *Figures 15 and 16* the ink penetration can be observed for each of these coatings. There is a quite low amount of ink penetration, and it is probably only the ink pigment and the resinous binder which is being seen, as the water solvent would not be imaged using this technique. However but it can clearly be seen, that it is greater for the PCC coating. There is also a thinner amount of ink remaining on the paper surface, and this would relate to the lower measured print density.

### Addition of Kaolin

In practice, sole pigments are rarely used in a coating formulation and using a blend of different minerals is often the most practical approach for optimisation of coating and printing properties. For this reason blends of 3 different partner clays were made with the PCC pigment at 12 pph binder level.

*Table 3* summarises the paper properties for all of the pigment combinations at 12 pph binder.

There is a slight synergy observed for the PCC / platey kaolin pigment blend with an slightly higher brightness and whiteness, probably due to increased light scattering from disrupted particle packing.

Addition of a partner clay to the PCC has resulted in a lower macro-roughness than the 100% PCC and a slightly higher RI *(Figure 17)*, and the combination of these has increased the sheet gloss further.

Addition of the clay to the PCC coating considerably decreases its porosity, resulting in a far longer stain length, and a higher RI (surface porosity), as shown in *Figure 17*. Interestingly, there is very little differentiation between the coatings with different types of clay added. It is likely that the fine clays are simply filling up the holes between the PCC particles.

In *Figure 18* the relationship between print delta gloss (print gloss minus paper gloss) and its relationship to the stain length results is shown. There is clearly a good correlation between the stain length and the delta gloss, with a long stain length (lower porosity surface) giving a higher print delta gloss. This may indicate that there is no loss in delta gloss with addition of clay, but an increase in ink mileage as shown by the stain length increase.

Despite the decrease in porosity of the samples on addition of kaolin, there was unfortunately no measurable increase in the print density, as shown in *Figure 19*.

## Discussion

This work has outlined some of the most important coating structural properties for flexo printing of coating linerboard.

The choice of coating pigment has a major impact on the coating structure and properties of the final board. 100% PCC gave a high gloss surface and a high brightness and whiteness. Addition of a partner kaolin did not reduce the optical benefits of this coating significantly. Indeed some synergies in optical properties were observed when a platey kaolin was combined with the PCC.

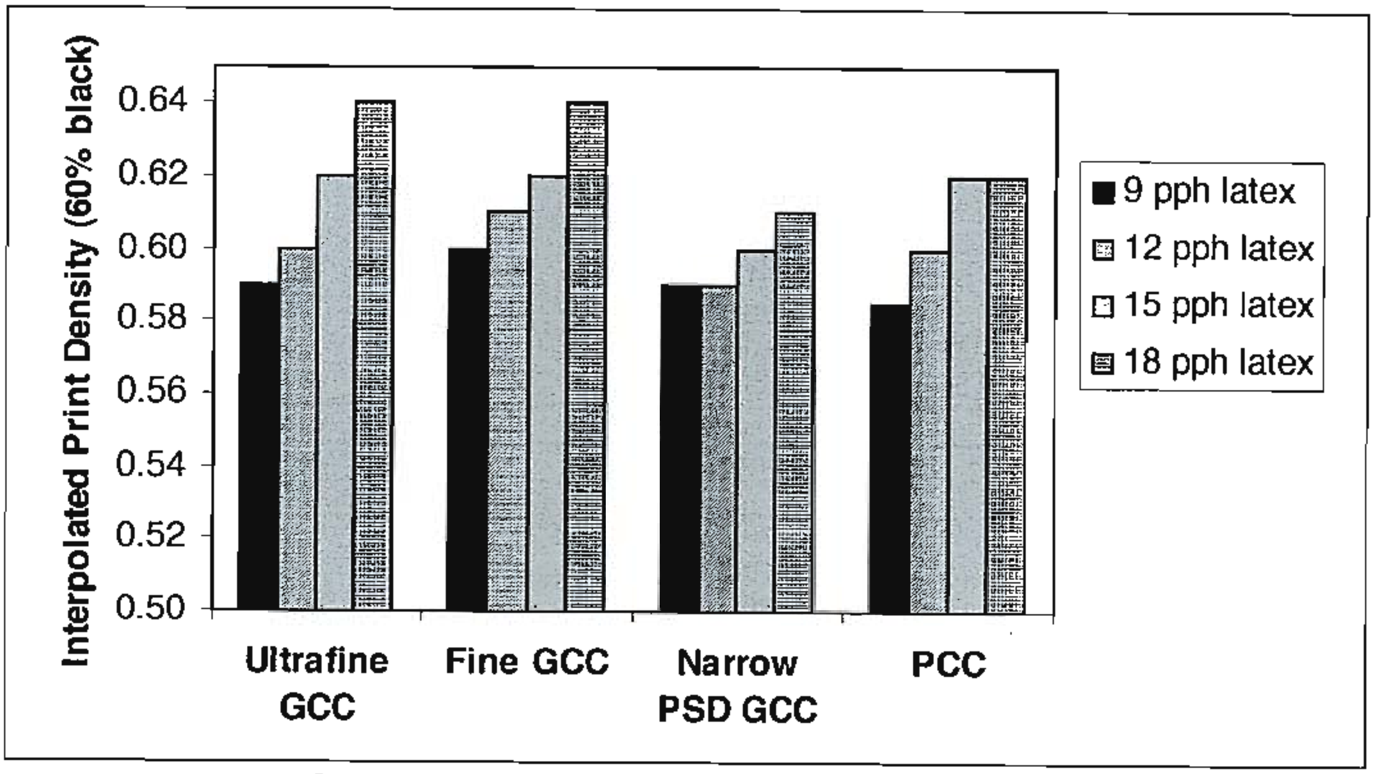


Figure 14 Black print density for different pigments and binder levels

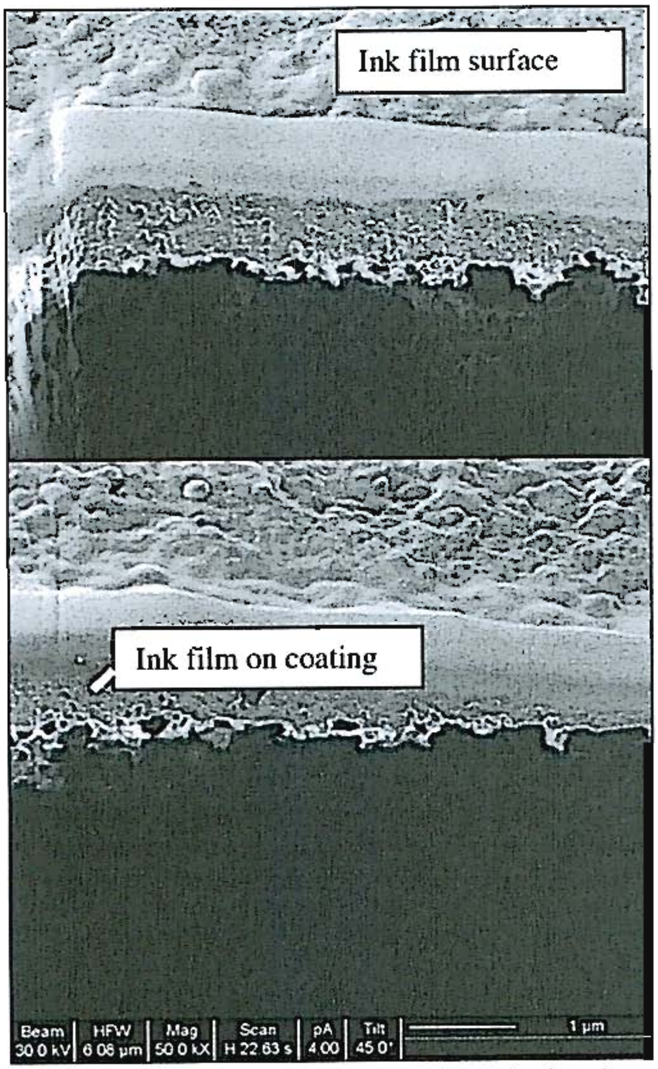


Figure 15 Very little Z direction ink penetration into the Ultrafine GCC coating. 9 pph latex

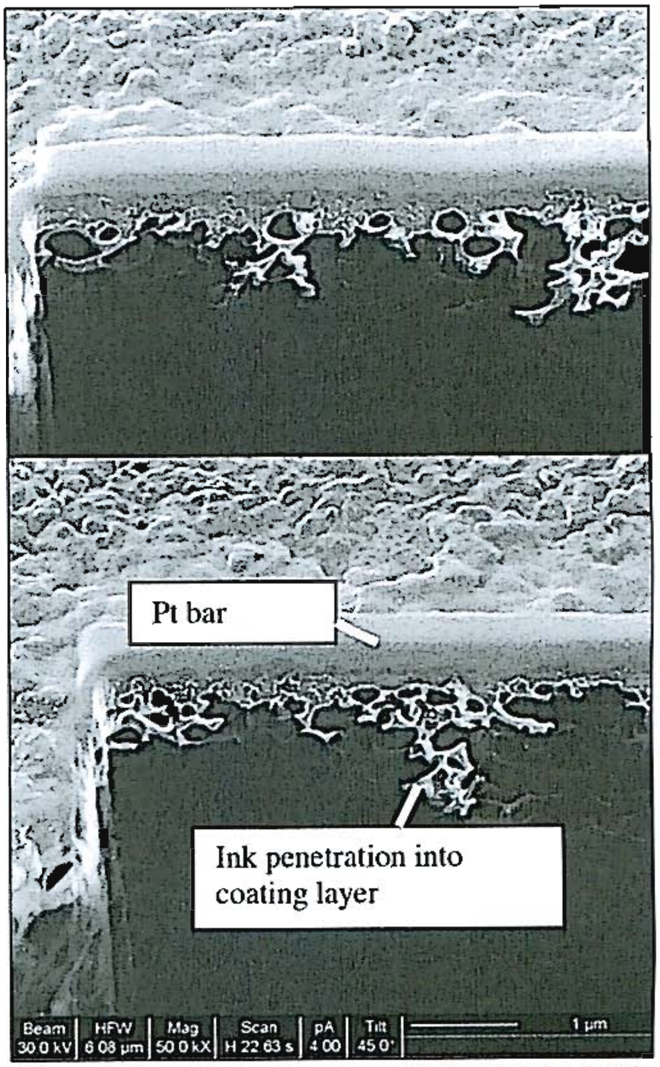


Figure 16 More Z direction ink penetration into the 100% PCC coating. 9 pph latex

| Cal 80°C and 50 kN/m | Tappi Gloss | Brightness | L* | a* | b* | Whiteness | PPS / µm |
|---|---|---|---|---|---|---|---|
| | 75° / % | | D65 with 400 nm UV filter | | | | 1000 kPa |
| Ultrafine GCC | 50.4 | 79.6 | 91.8 | -0.21 | 0.78 | 76.6 | 1.99 |
| Fine GCC | 41.9 | 78.8 | 91.4 | -0.23 | 0.81 | 75.5 | 2.07 |
| Narrow PSD GCC | 52.6 | 80.8 | 92.1 | -0.22 | 0.45 | 78.9 | 1.89 |
| PCC | 55.0 | 81.1 | 92.3 | -0.24 | 0.48 | 79.2 | 1.73 |
| PCC/Platey kaolin | 58.3 | 82.0 | 92.6 | -0.25 | 0.39 | 80.4 | 1.75 |
| PCC/Fine platey kaolin | 58.0 | 80.9 | 92.2 | -0.27 | 0.48 | 78.9 | 1.52 |
| PCC/Fine blocky kaolin | 58.3 | 80.7 | 92.1 | -0.28 | 0.55 | 78.5 | 1.83 |

| Cal 140°C and 25 kN/m | Tappi Gloss | Brightness | L* | a* | b* | Whiteness | PPS / µm |
|---|---|---|---|---|---|---|---|
| | 75° / % | | D65 with 400 nm UV filter | | | | 1000 kPa |
| Ultrafine GCC | 50.0 | 79.2 | 91.6 | -0.21 | 0.84 | 76.0 | 1.87 |
| Fine GCC | 45.1 | 79.2 | 91.6 | -0.21 | 0.71 | 76.4 | 1.76 |
| Narrow PSD GCC | 54.6 | 80.8 | 92.2 | -0.22 | 0.48 | 78.9 | 1.82 |
| PCC | 56.2 | 81.6 | 92.5 | -0.23 | 0.42 | 79.9 | 2.00 |
| PCC/Platey kaolin | 58.3 | 82.0 | 92.7 | -0.24 | 0.41 | 80.4 | 1.59 |
| PCC/Fine platey kaolin | 58.6 | 81.2 | 92.3 | -0.26 | 0.47 | 79.3 | 1.61 |
| PCC/Fine blocky kaolin | 59.0 | 80.7 | 92.2 | -0.28 | 0.56 | 78.5 | 1.76 |

Table 3. Paper properties for coatings at 12pph binder level

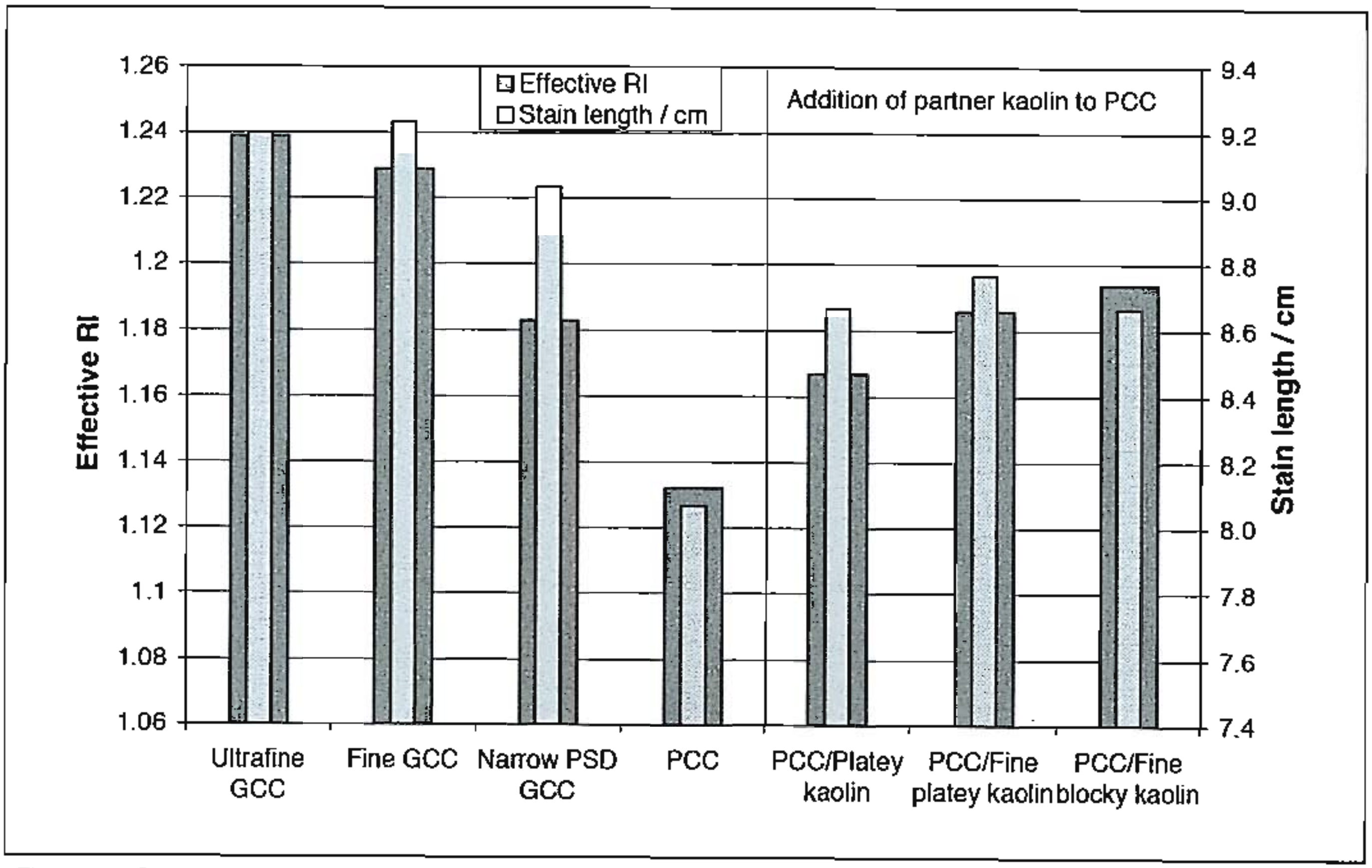


Figure 17. Bulk porosity (stain length) and surface porosity (RI) of coatings containing 12 pph binder. Addition of a partner kaolin to the PCC decreases the porosity.

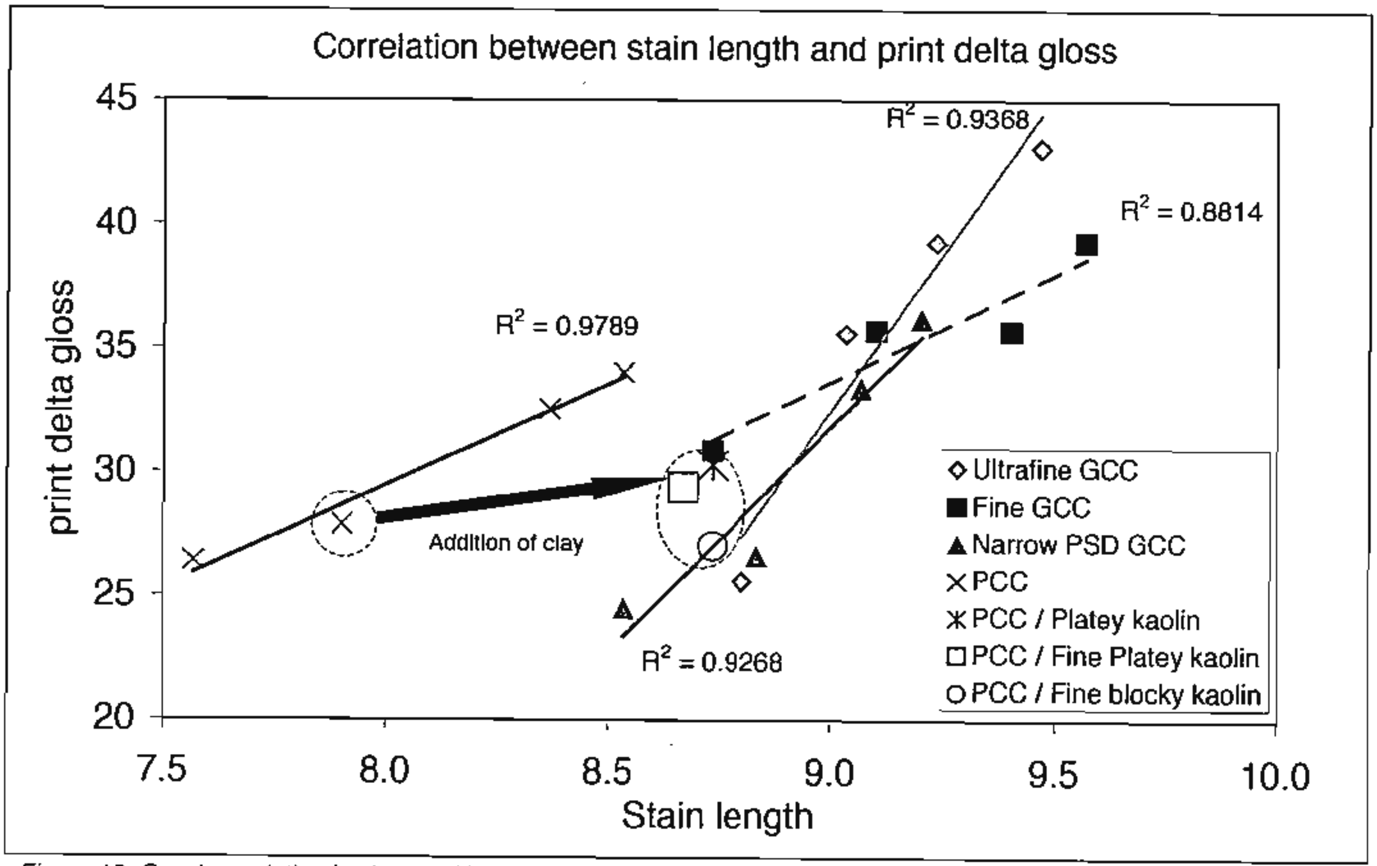


Figure 18. Good correlation is observed between the stain length and the print delta gloss for each pigment / binder system. Addition of a platey partner clay to the PCC coating has closed up the surface and improved the print delta gloss.

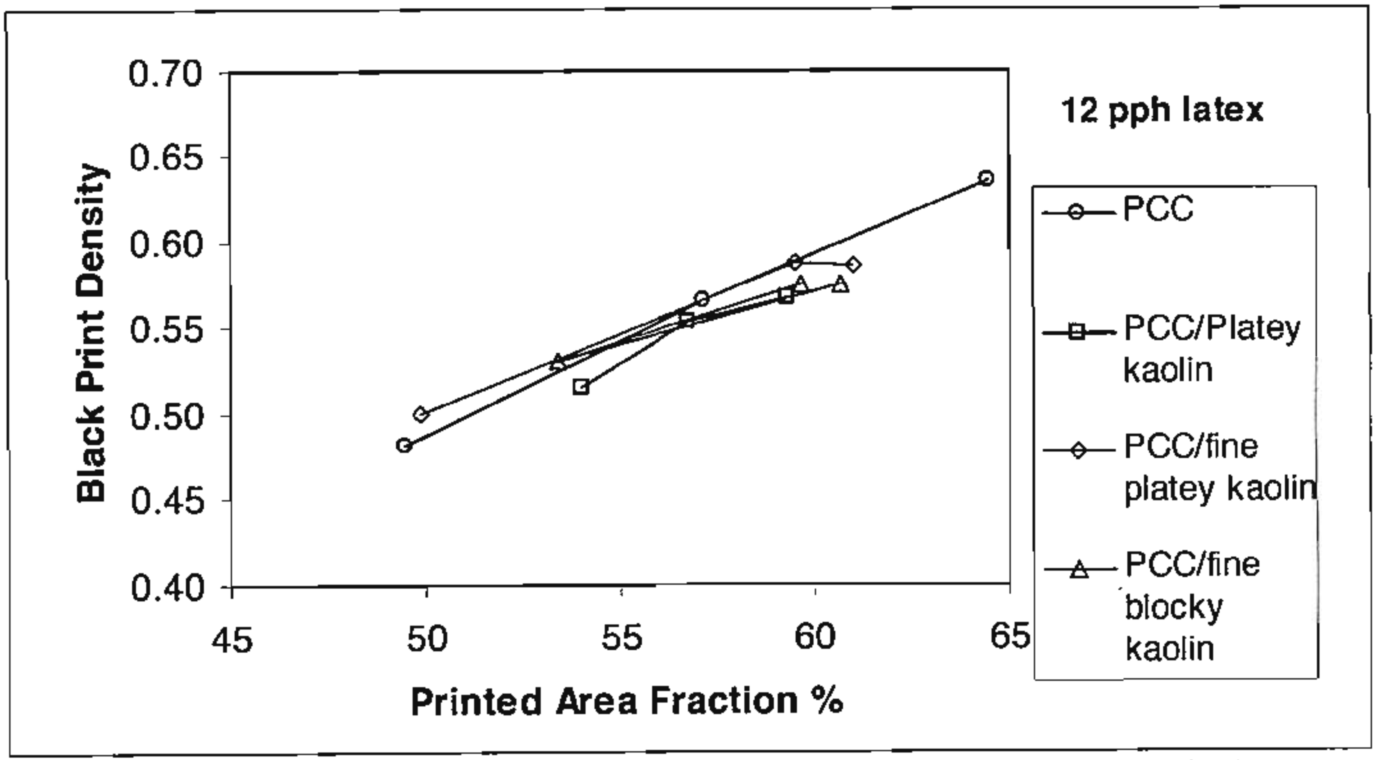


Figure 19. Print density for PCC coating and PCC with partner kaolin, as a function of printed area fraction.

The stain length test clearly showed the differences in surface porosity between the different pigment coatings. The PCC was the most open, followed by the Narrow PSD GCC. The broad GCC samples had the lowest surface porosity. Calendering temperature also influenced the porosity with a higher calendering temperature giving a more closed surface and longer stain lengths.

In flexo printing, one of the most important quality parameters is that the dot gain is even from point to point. The printer can compensate on press to achieve a certain dot gain and a print with the required colour and print density. However an uneven spread of ink from point to point on the substrate will result in mottle. Another important criterion for flexo printing is fast drying of the ink to avoid smearing and bleeding of the colours. Hence fast adsorption of the fluid phase of the ink into the coating layer is desirable. However, it is important to keep the coloured portion of the ink on the surface of the print to avoid low colour density or an increase in ink consumption. The print results from this study indicated that a slightly higher print gloss and density were achieved on substrates where the ink was better held on the surface, i.e. a broad particle size distribution carbonate, and one with a higher latex level. For these coatings the ink spread further giving a higher total printed area in the halftone region, and a higher print density. In reality this may allow the printer to use less ink to achieve his desired dot gain. A porous coating, such as 100% PCC, gave smaller dots, a lower print density and a higher ink penetration in the z direction. However addition of a partner clay, either the fine platey kaolin or the coarser platey kaolin filled up some of the surface pores and lowered the porosity. This was achieved without loss of the optical benefits afforded by using a narrow particle sized distribution carbonate. Addition of a platey partner kaolin to the PCC resulted in an increase in the print gloss, but unfortunately no measurable increase in print density for the same area of print coverage.

The calendering appeared to have little real impact on the paper and print properties in this case, although the stain length tests indicate that the higher temperature resulted in a slightly more sealed surface. It is possible that altering the calendering conditions may have effected a greater change in the basepaper than the coating layer.

## Conclusions

This work has shown the following:

- Coating structure of coated board can be influenced considerably by the choice of pigment in the coating layer. Narrow particle size pigments produce a more open coating with better optical properties.
- The 100% PCC coating has a very porous coating which resulted in higher ink penetration in the z direction and a lower print gloss and density.
- Addition of a partner kaolin to the PCC can reduce the porosity of the coating layer.
- As a secondary effect the coating structure can also be varied by using different amounts of binder. A higher binder content gives improvements in ink hold out, but is slightly detrimental to the paper optics. However sufficient binder (high levels) is required to prevent common board problems such as cracking during the creasing process, which was not studied in this exercise.
- Altering the finishing conditions is another tool for the paper maker, although altering the calendering temperature appeared to have little impact on the optical and printing properties of the coated boards in this study. This may have been impacting the basepaper rather than the coating layer.
- It may be the case that the optimum balance of properties is achieved using a multi-pigment blending approach. Combining a PCC with a fine platy kaolin maintains a coating with a high optical performance as well as giving a good surface on which to print.

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## NOTES

# NOTES

# Use of a Steric Stabiliser as Water Retention Aids for Maximising Calcium Carbonate Use in Glossy Coated Paper

SESSION TWO

PAPER SEVEN

*by*
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## Abstract

Over the last few years, the use of clay in glossy coated paper has declined. This has been driven both by the need to produce brighter papers and further by increasing cost and declining availability of clay. This has increased interest in calcium carbonate. This paper describes the use of a steric stabiliser as a water retention aid to decrease the aggregation of particles in coating structure. Improved coating structure order has been found to improve gloss and thus reduce the need for clay. Traditional water retention aids function by increasing the viscosity of the dispersing medium. However, as the solids increase during coating application and drying the pigments can aggregate causing a non-even structure to form, which reduces gloss. This new class of water retention aids are polymers with a structure of steric stabilisers. These improve water retention by decreasing the amount of free water in the system. The polymers also prevent aggregation during coating application and drying so a good state of dispersion of the particles is kept causing improved gloss. Examples of this technology in pilot and full-scale mill application are given.

## Introduction

Coating colours are concentrated suspensions of solid particles in a water based liquid phase. The solids particles can be mineral or organic. The mineral particles are the pigments (calcium carbonate, clay, talcum) and the organic ones are mainly the latex or in some cases also plastic pigments. The liquid phase contains dissolved substances: ions and organic polymers. The dissolved organic polymers can be of low or high molecular weights and originate from natural or synthetic products. They can also be strongly anionic or non-ionic and very seldom cationic. These dissolved organic polymers are introduced for many purposes including rheology control (dispersing agents and thickeners), brightness increase (OBA), insolubilisation, shading, and defoaming. This being said one can understand that coating colours are complex mixtures in which all the constitutive components may interact. Well-dispersed slurries of pigments, which means at their optimum of high solids content with low viscosities, and well-stabilised dispersions of lattices are mixed together and sheared in a liquid phase that receive increasing amounts of dissolved substances during the coating colours preparation. The equilibrium between the dispersive and the attractive forces may be changed and cause formation of particles agglomerates. Viscosity is a consequence and a reflection of the pigments and lattices particles state of dispersion. For a given system of solid particles at a given solids content, low viscosity levels can be assimilated to a good state of dispersion and higher viscosity levels to the very possible presence of particles agglomerates. The formation of particles agglomerates is a major means for the thickeners to increase the viscosity of coating colours. The presence of these agglomerates can be detrimental for both the rheology and the paper surface. The use of steric stabilisation technology, instead of classic thickeners, can improve runnability, paper smoothness and gloss. Viscosity remains a major parameter of the paper coating process and regulates blade pressure and water retention.

## The Role of Viscosity in the Paper Coating Process

Rheology modifiers a can influence a coating colour during pumping, filtration, deaeration and the behaviour under a blade or in a film press nip, where the coating colour is submitted to plane shearing or to stretch. These account for less than one percent of the coating colour and less than five percent of the formulation costs. When they are well chosen to fit to a given coating colour applied with a given coating technology significant cost savings can be achieved.

### Viscosity and Water Retention

The liquid phase migration into the absorbent base paper should be under control. In blade coating, a too fast migration creates a gradient of concentration in the coating colour thickness during the dwell time. An immobilised layer of pigment will grow from the base paper surface and eventually reach the surface in contact with the blade. The solids content right under the blade tip can then be high and close to the immobilisation solids where the coating colour switches to dilatancy. The blade load and the blade wear will be increased. Risk of bleeding increases. Fines and latex particles migration carried by the flow of the liquid phase will leave the coarser pigment particles at the surface with a deficit of binder. Decreased gloss and dusting are some of bad consequences from too low water retention.

The Darcy and the capillary ascension laws describe with simple equations the contribution of viscosity in the liquid phase penetration. The base paper pores are assumed to be capillaries.

The Darcy law: $\frac{Q}{A} = \frac{K_v \times \Delta P}{\eta \times L}$

$Q$: Flow of fluid through a porous medium with a thickness $L$
$A$: Surface of contact
$K_v$: Permeability coefficient of the porous medium
$\Delta P$: Pressure gradient through the thickness $L$ of the porous medium
$\eta$: Viscosity of the liquid

The capillary ascension law: $h^2 = \frac{r \times \vartheta \times \cos\sigma \times t}{2\eta}$

$h$: height of the liquid in the capillary at time $t$
$r$: radius of the capillary
$\vartheta$ : Surface tension of the liquid
$\sigma$: Contact angle liquid/capillary wall
$t$: time of contact liquid/capillary

Higher values of the liquid phase viscosity slow down its penetration. The liquid phase surface tension as well as the notions of sizing degree and permeability of the porous and absorbent base paper are also mentioned here.

**Viscosity and blade pressure**

Aside friction and compression forces related to the base paper compressibility or the backing roll hardness, three forces exerting on the blade can be linked to the coating colour (*Figure 1*)[11]:

- Impulse forces $F_i$ from the jet of coating colour striking the blade and being deviated for recirculation in the circuit:

  $F_i = mU(1+\cos\theta)/\sin\theta$ (Eklund)

  m: coating colour mass flow (kg/s) striking the blade
  U: coater speed (m/s)
  θ: coating head angle
- Hydrodynamic forces $F_h = \frac{6\eta U}{\tan^2\theta} \times \left( \ln\left(\frac{h_1}{h_2}\right) - 2\left(\frac{h_1 - h_2}{h_1 + h_2}\right) \right)$

  $h_1$ and $h_2$ : thickness of the coating colour film before and after the blade
  $\eta$: coating colour viscosity for the shear rate under the blade
- Shear forces: $F_{Sh} = \gamma \times \eta \times S_{tip}$

  where $S_{tip}$ is the area of the blade tip in contact with the coating colour
  $\gamma$ is shear rate
  $\eta$ is viscosity

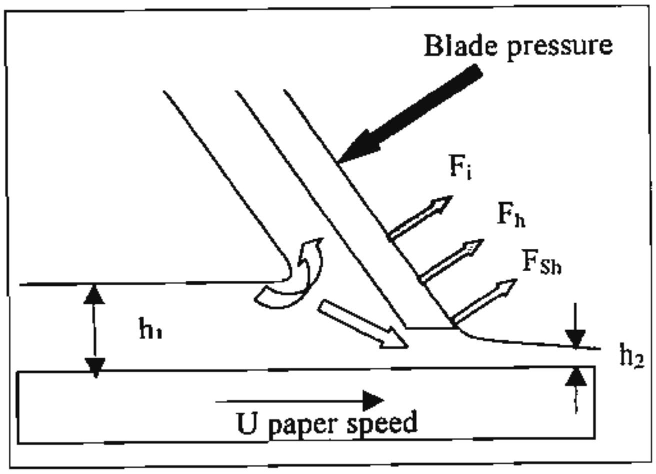

Figure 1 Forces acting on the blade

Higher blade loads, or higher coat weights for a given blade load, can be reached with increased high shear viscosities either by means of a higher solids content (*Figure 2*) or with the addition of a chosen thickener (*Figure 3*).

The J.M.Kuzmak equation expresses also the role of viscosity in coat weight control:

$$h_t = h' + K_1 \sqrt{\frac{K_2 \times 6\eta S^2 U \times \cos\theta}{KP_G - a_1 F_m}}$$

$h_t$ wet coating thickness
h' Minimum coat weight
$\eta$ Viscosity of coating colour
S = C/sinθ
U Speed
C Blade thickness
θ Blade angle
$P_G$ Blade pressure
$F_m$ Hydraulic forces exerted by the coating colour flow
$a_1$, K Conversion coefficients
$K_1$,$K_2$ Constants

**Viscosity and misting on Metering Size Press**

At the exit of the MSP nip, the coating colour is stretched and not sheared.

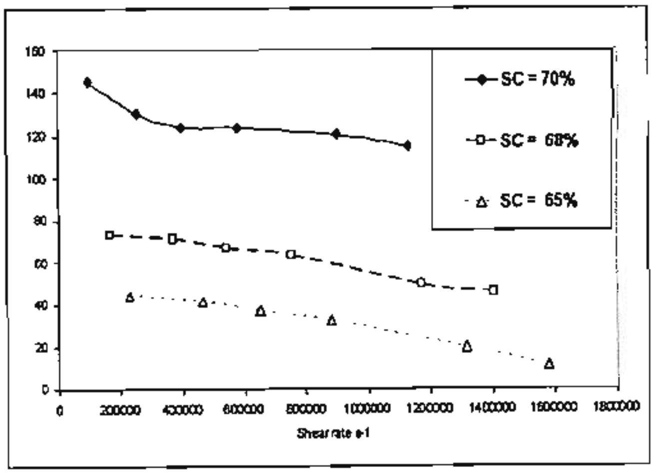

Figure 2 Capillary viscosity as a function of solids content

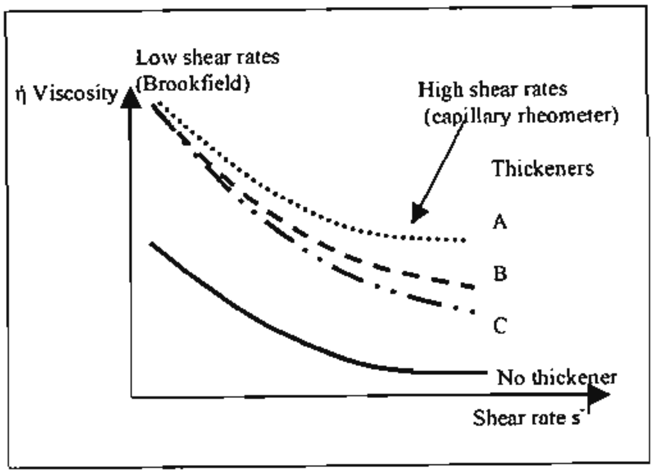

Figure 3 Capillary viscosity as a function of thickeners type

The misting trend is often linked to the viscoelastic behaviour of the coating colour. As seen in the oscillatory viscometry graph below, a strain resistant elastic modulus G' can be detrimental. The coating colours for which the phase angle switches from below 45° (G'>G") to over 45° (G">G') at lower strain are less prone to misting *(Figure 4)*.

G" is the viscous or loss modulus.

## Viscosity and Paper Quality

As already mentioned before, water retention drives the coating colour hold out and is itself driven by the coating colour viscosity or more precisely the liquid phase viscosity.

In that sense the viscosity influence on paper quality is a well-established fact. Nevertheless, viscosity is also a clue of good or bad particle's state of dispersion and their consequences for the paper surface.

**Viscosity reflecting the coating colour structure.**

*Newtonian systems*

In a Newtonian system, viscosity is a constant and does not depend upon the applied shear.

It can be temperature dependant. A simple way to link the viscosity with the physics of particles dispersion is to consider the Einstein (1906) law[2]:

$$\eta = \eta_0(1 + 2.5 \times \Theta)$$

$\eta_0$ is the liquid phase viscosity

$\Theta$ is the volume fraction of the particles (sum of the particles volume divided by the total volume of the dispersion)

The Einstein law applies to diluted suspensions with the following conditions:

- the particles are non interactive mono dispersed hard spheres
- the liquid phase is Newtonian

Still it already predicts the viscosity increase with the solids content (higher volume fraction) and with the liquid phase viscosity.

At higher solids or for higher volume fractions Krieger-Dougherty (1959) and Maron-Pierce (1956,1981) introduce the notion of maximum close packing volume fraction $\Theta_m$

$$\eta = \eta_0\left(1 - \frac{\Theta}{\Theta_m}\right)^{-2}$$

$\Theta_m$ is the maximum volume of particles that can be introduced per unit volume of the suspension.

It takes into account the particles shapes and size distributions. At high solids content when the volume fraction reaches $\Theta_m$, the accumulation of particles is such that no further movement is possible. Viscosity tends to infinite. This notion can be linked to the immobilisation solids.

*Non-Newtonian systems*

For most of the mineral suspensions in water, including the coating colours, viscosity is not constant. At least below their immobilisation solids coating colours are thixotropic and shear thinning which means that viscosity decreases with time and applied strains. Coating colours differ from the upper models of Newtonian systems because:

- the particles are polydispersed
- there are strong interactions between the particles
- the liquid phase may not be Newtonian

*Effect of the particles sizes polydispersion on viscosity*

Coating colours are concentrated dispersions of poly-dispersed particles. The latex particles rank between 0.1 and 0.2 microns. Coating pigments have a Gaussian particles size distribution with a mean diameter from 0.4 micron, for the finest grades, up to 3-4 microns for the coarser ones. The effect of polydispersity on viscosity can be found by referring to the previous Krieger-Dougherty-Maron-Pierce equation. Smaller

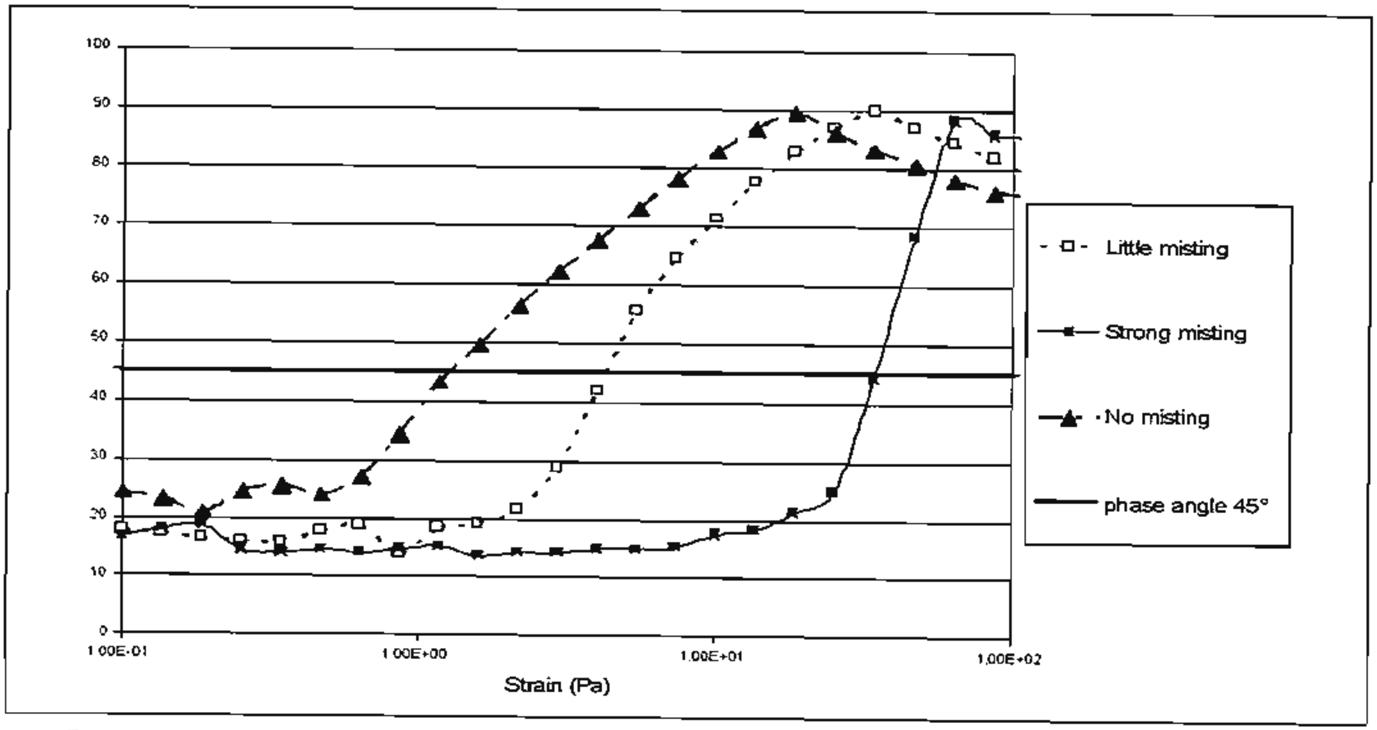

Figure 4 Phase angle α evolutions vs Strain (oscillations – 1 Hz) for three coating colours and their misting trends

particles can fill up the voids between the coarser ones. Thus, $\Theta_m$ is increased and viscosity decreased. Narrow particles size distribution pigments lead to higher viscosities than equivalent pigments, in terms of fineness.[3]

*Effect of particles interactions on viscosity*

The balance of forces between particles can lead either to the formation or to the destruction of agglomerates. Agglomerates are assumed to be a coherent ensemble which volume fraction is the addition of the particles volume fraction plus the volume of the entrapped liquid phase between the particles.

$$\Theta_{agg.} = \Theta_{part.} \times N^{\frac{3-D_f}{D_f}}$$

$\Theta_{agg.}$ is the volume fraction of the agglomerate
$\Theta_{part.}$ is the volume fraction of one particle.
$D_f$ is the fractal dimension of the agglomerate.
N is the number of particles in the agglomerate.

As consequence, an agglomeration means an increased volume fraction and a higher viscosity or reciprocally, the break down of the agglomerates ends up with a lower volume fraction and a reduced viscosity.

**Forces acting on particles in Non-Newtonian suspensions[4]**

*Hydrodynamic forces - Viscosity measurement*

The hydrodynamic forces stem from the process when the coating colour is under agitation in the storage tanks or pumped or filtered or sheared under a blade. They are responsible for the total or partial breakdown of the particles agglomerates. The resistance of the agglomerates to their own destruction or their ability to stretch and deform under the hydraulic forces are at the origins of thixotropy, yield stress and viscoelasticity.

Measuring viscosity consists in the evaluation of these rheological characteristics. In principle, a rheometer applies hydrodynamic forces (a shear stress) in a given geometry at measured speeds *(Figure 5)*.

By definition viscosity: $\eta = \tau \times \frac{\partial u}{\partial y}$

| | |
|---|---|
| $\tau$ | Shear stress in Pascal |
| $\partial u/\partial y$ | Shear rate in $sec^{-1}$ |
| $\eta$ | Viscosity in Pa.s |

The hydrodynamic forces in the rheometer chamber put the suspension into motion and may break down existing agglomerates of particles.

We should also mention here the migration model of Acrivos[5] as an alternative to describe thixotropy. According to this model, migration of particles can occur in two cases:

- Sedimentation of the heavier (coarser) particles submitted to gravitational forces and described by the Stoke's law:

$$V_{sed} = 2a^2 g\left(\frac{\rho_{part.} - \rho_{liq}}{9\eta}\right)$$

a is particle radius
g acceleration
$\rho_{part}$ and $\rho_{liq}$. the particle and the liquid phase densities
$\eta$ viscosity

- Migration under shear

Particles move to the region with the lower shear rates or in other word migrate from the moving to the stationary boundaries of the rheometer.

The migration model seems to focus more on the measurement of viscosity with long time scales and low shear rates. It is controversial whether it can apply to coating colours of high viscosities, high solids and under continuous agitation.

*Non-hydrodynamic forces*

The non-hydrodynamic forces between particles are:

- The Brownian motion
- The Gravitational forces
- The London-Van der Waals (LVdW) attractive forces
- The Electrostatic repulsive forces
- The Steric repulsive forces

The Brownian motion originates from the fluid thermal energy. A permanent agitation of the fluid molecules carries the smaller particles. These forces are negligible for particles over one micron and for concentrated dispersions in which the electrostatics forces are much bigger. The gravitational forces can taken into consideration during sedimentation of low viscosity slurries left without agitation. They can be neglected in the case of highly viscous coating colours under permanent motion.

The attractive London-Van der Waals forces originate from interactions between the surface dipoles of the particles.

The attractive energy $V_A$ between two spherical particles:

$$V_A = \frac{-A \times a}{12h_0}$$

- A is the Hamaker constant integrating all the dipole interactions
- a is the spheres radius
- h is the distance between the spheres
- $h_0 = h - 2a$ smallest distance between the spheres

The electrostatic repulsive forces occur when two particles are of the same electrical sign. These Coulombian forces depend upon the Debye length *K* corresponding to the thickness of the fixed layer of the liquid phase that surrounds each particle. This layer is highly ionic.

The repulsive energy $V_R$ between two spherical particles:

$$V_R = 2\pi\varepsilon\varepsilon_0\psi^2 K \times a\left(\frac{e^{-(1/K)h}}{1+e^{-(1/K)h}}\right)$$

- h distance between the spheres
- $\varepsilon\varepsilon_0$ electric permittivity
  $\psi$ Surface potential
- K Debye length
- K :$\propto\sqrt{kT/2I}$
- k Boltzman constant
- T temperature
- I ionic strength of the media
- a radius of the spheres

Strongly anionic dispersing agents adsorb on the particles surface and modify the Debye length. Selected molecular weights and addition rates of dispersing agents maximise the repulsive energy in order to maintain the state of dispersion and minimise viscosity.

The total energy $V_T = V_A + V_R$ resulting from the attractive L-VdW forces and the repulsive electrostatic forces can be:

- positive and the particles remain dispersed
- or negative and the particles flocculate

According to the DLVO theory $V_T$ as a function of the distance h between two particles, can become negative for small values of h *(Figure 6)*. In other words, when two particles are close enough the repulsive forces are lower than the attractive forces and the particles can flocculate.

When are the inter particles distances reduced and the risk of flocculation high?

- At higher solids content

High solids can be a choice already at the coating colour preparation but high solids will definitely occur during the dewatering and the drying phases of the coating colour.

- With finer particles

Reduced inter particle distances and in the mean time higher charge density and higher mobility make the fine particles more prone to flocculation.

The viscosity increase with higher solids or finer particles comes from an increase of the volume fraction. Increased volume fractions can stem from a bigger mass of solid particles or the previous notion of the agglomerates volume fraction ðagg if the particles flocculate.

## Introduction of Steric Stabilisation in Paper Coating

### Steric Stabilisation

Steric stabilisation is a known technology for the stabilisation of colloidal particles by non-ionic macromolecules[6][7][8]. It consists in adsorbing a layer of non-ionic macromolecules on the surface of the particles to disperse. The best effective polymers are made of anchor groups firmly attached to the particles surface and stabilising moieties soluble in the liquid phase.

When two steric stabilised particles approach each other, the adsorbed layers of polymers resist to inter-penetration *(Figure 7)*.

The Gibbs free energy change during the attempt of overlapping of the adsorbed layers can be written:

$$\Delta G = \Delta H - T \Delta S$$

Where $\Delta H$ and $\Delta S$ are the variations of enthalpy and entropy – T is the temperature.

When $\Delta G$ is positive, the particles remain dispersed.

When $\Delta G$ is negative, the particles flocculate.

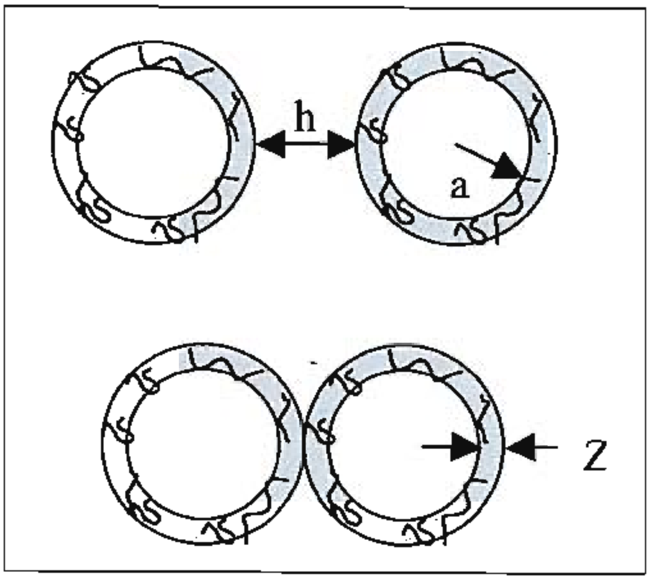

Figure 7 Approaching steric stabilised particles with their layers of polymers

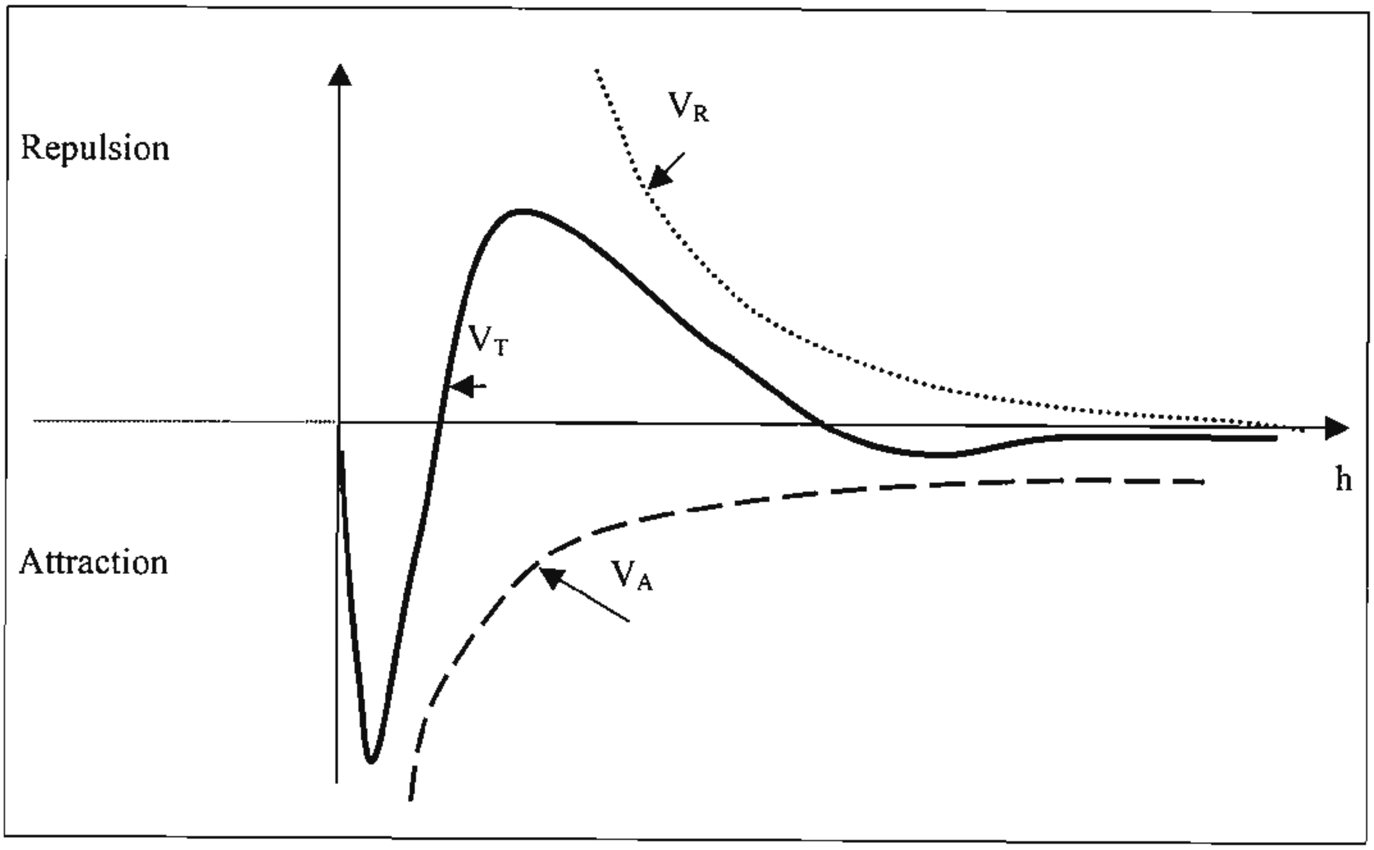

Figure 6 DVLO theory – Attractive and Repulsive energy as a function of inter particle distance h

The system switches from stabilisation to coagulation for a critical temperature $T_c$.

The steric stabilisation energy VS as given by Napper (1983)(4):

$$V_S = akT\frac{Z^2\left(\frac{1}{2}-\chi\right)}{h_S v_S}$$

a is the particle radius
k the Boltzmann constant
T the temperature
$\chi$ the interaction factor between the stabiliser and the liquid phase
Z the thickness of the polymer layer
$h_S$ a function of the particles distance
$v_S$ the molar volume of the liquid phase.

Steric stabilisation can be an additional repulsive energy to the total energy rendering the risks of flocculation lower:

$$V_T = V_A + V_R + V_S$$

Steric stabilisation also induces some viscosity increase. An effective volume fraction can be calculated for each particle with a radius a + Z including the attached polymer layer:

$$\Theta_{eff} = \Theta_{part.}\frac{(a+Z)^3}{a^3}$$

**Design of a Steric Stabiliser as rheology modifier and water retention aid**

Classic thickeners are hydrophilic polymers that can increase viscosity and provide water retention by two means:

- Absorption and jellification of the liquid phase increasing $\eta_0$
- Formation of particles agglomerates in order to increase the apparent volume fraction.

The agglomerates are either a consequence of depletion flocculation (when the liquid phase is absorbed by the polymer and deficient around the particles (PAC Gane,(9)) or the thickeners ability to bridge between adjacent particles. The carboxylic groups of synthetic thickeners can adsorb on the pigment surface. The additional hydrophobic groups of associative thickeners can also react with the hydrophobic surface of the latex particles and create more agglomerates. The longer the polymers chain, the bigger the agglomerates, the higher the elasticity and the high shear viscosity.

Classic thickeners have drawbacks linked to their thickening mechanism:

- Formation of agglomerates causing a rougher paper surface and lower gloss
- Strong increase of the Brookfield viscosity needed to improve water retention
- Increased elasticity
- No OBA carrying effect of the synthetic thickeners

New high molecular weight polymers designed as weakly anionic steric stabiliser can surround each pigment particle with a thick hydrolysed layer. These polymers can provide the following benefits.

- Steric stabilisation protects particles from flocculation even at high solids content
- A moderate increase of Brookfield viscosity
- A good water retention
- A low elasticity
- An OBA carrying effect

## Case Studies

In the following case studies some examples will be shown, where steric stabiliser has been used in different coating trials (pilot and mill). In all of the trial formulations CMC has been replaced totally with a steric stabiliser. At the same time solids content and the share of carbonate have been increased.

**CASE 1: Replacement of CMC (GCC 90 % < 2 um, Steric Stabiliser 1)**

In this pilot trial, the use of the steric stabiliser as a water retention aid was examined by coating 58 g/m² basesheet with 12 g/m² of coating using a blade coater. The formulations used and the key paper quality results are given below. This trial showed a significant increase in gloss with some loss in optical properties.

| | | |
|---|---|---|
| Fine GCC, pph | 80 | 80 |
| Fine US clay, pph | 20 | 20 |
| Latex, pph | 11 | 11 |
| OBA, pph | 0.8 | 0.8 |
| CMC, pph | 0.3 | |
| Steric stabiliser 1, pph | | 0.5 |
| 75° Gloss, % | 58 | 63 |
| 75° Print Gloss, % | 65 | 70 |
| % Brightness +UV | 98.6 | 97.7 |
| % Brightness -UV | 85.4 | 85.0 |
| % Opacity | 86.6 | 86.0 |

Case study 1: Replacement of CMC with Steric Stabiliser 1

Some Questions were then raised:

Would the Rheocarb work in a more demanding situation, a double-coated sheet with finer carbonates? Could this increase in gloss be used to eliminate the use of clay?

Would this reduction in clay eliminate the slight loss in optical performance?

**CASE 2: Replacement of clay (GCC 95 % < 2 um, Steric Stabiliser 1)**

Another trial was run applying 12 g/m² of coating onto an 80 g/m² precoated sheet. Again, coating formulations and key paper results are given below. This showed that use of the steric stabiliser would prevent the gloss loss caused by removing 20 parts of clay. By eliminating the clay, the brightness could be improved over the original formulation but there was still a slight loss of optical properties when comparing CMC to the steric stabiliser in equivalent formulations.

| | | | | | | |
|---|---|---|---|---|---|---|
| Ultrafine GCC, pph | 80 | 100 | 100 | | | |
| Coating PCC, pph | | | | 80 | 100 | 100 |
| Fine US clay, pph | 20 | | | 20 | | |
| Latex, pph | 11 | 11 | 11 | 11 | 11 | 11 |
| PVA, pph | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 | 0.4 |
| OBA, pph | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| CMC, pph | 0.3 | 0.3 | | 0.3 | 0.3 | |
| Steric stabiliser 1, pph | | | 0.45 | | | 0.45 |
| 75° % Paper Gloss | 84 | 79 | 83 | 85 | 81 | 85 |
| 75° % Print Gloss | 84 | 80 | 79 | 82 | 74 | 74 |
| % Brightness +UV | 99.4 | 103.0 | 101.6 | 98.6 | 101.4 | 101.0 |
| % Brightness -UV | 85.7 | 87.4 | 86.8 | 84.6 | 86.2 | 85.8 |
| % Opacity | 90.0 | 90.0 | 89.5 | 89.6 | 89.6 | 89.4 |

Case Study 2: Replacement of clay in gcc and pcc containing formulations

### CASE 3: Replacement of clay (GCC 95 % < 2um)

This approach was then trialled at woodfree double coated mill. This showed that loss in gloss by removing 15 parts of fine clay could be stopped through increasing solids and use of steric stabiliser 1. This reduction in clay meant there was an increase in brightness.

| | Reference formulation | Clay replacement with CMC | Clay replacement with Steric Stabiliser 1 |
|---|---|---|---|
| GCC 95 % < 2 um | 85 | 100 | 100 |
| Fine clay | 15 | | |
| Latex SBR | 11 | 10.5 | 10.5 |
| CMC | 0.3 | 0.3 | |
| PVOH | 0.4 | 0.4 | 0.4 |
| Steric Stabiliser 1 | | | 0.45 |
| OBA | 0.8 | 0.8 | 0.8 |
| Solids content % | 68.8 | 68.1 | 69.3 |
| Brightness R457 +UV | 97.7 | 99.2 | 99 |
| Gloss Tappi 75 | 74 | 69 | 75 |

Case 3: Clay replacement in a glossy top coat - Bent blade - 800 m/min - 16 g/m²

### CASE 4: Replacement of clay (GCC narrow particle size distribution 75 % < 1 um, Steric Stabiliser 2)

In another woodfree mill, the use of steric stabiliser was trialled with narrow psd carbonate. This mill needed a higher Brookfield viscosity so a different steric stabiliser was used. A pilot study showed that use of the steric stabiliser could improve the gloss and smoothness. This improvement in gloss could then be used to reduce clay use from 30% to 10% on this high speed coater.

| | Reference formulation | Study with Steric Stabiliser 2 | Clay replacement with Steric Stabiliser 1 |
|---|---|---|---|
| GCC narrow psd (75 % < 1 um) | 70 | 70 | 90 |
| Fine clay | 30 | 30 | 10 |
| Latex SBR | 12 | 12 | 12 |
| CMC | 0.6 | | |
| PVOH | 0.5 | 0.5 | 0.5 |
| Steric Stabiliser 2 | | 0.6 | 0.7 |
| OBA | 0.5 | 0.5 | 0.5 |
| Solids content % | 61 | 62.1 | 62.9 |
| Viscosity Br 100 rpm | 1050 | 870 | 930 |
| Water retention Gradek | 138 | 105 | 93 |
| Gloss Tappi 75 | 64.2 | 68.3 | 64.8 |
| Brightness R457 +UV | 93.4 | 93.2 | 94.8 |
| Opacity | 91.6 | 91.7 | 91.5 |

Case4: Clay replacement in a glossy top coat - Stiff blade - 1600 m/min - 9 g/m²

### CASE 5: Replacement of plastic pigment (GCC narrow particle size 75 % < 1 um, Steric Stabiliser 2)

Another mill was interested in using the steric stabiliser to eliminate the use of plastic pigment. The data below showed this could be done.

| | Reference formulation | Trial with Steric Stabiliser 2 |
|---|---|---|
| GCC narrow psd (75% <1 um) | 65 | 70 |
| Fine clay | 30 | 30 |
| Plastic pigment | 5 | |
| Latex SBR | 12 | 12 |
| CMC | 0.8 | |
| PVOH | 1 | 1 |
| Steric Stabiliser 2 | | 0.9 |
| OBA | 1 | 1 |
| Solids content % | 61 | 62 |
| Viscosity Bk 100 rpm | 1300 | 1200 |
| Capillary viscosity 106sec-1 | 140 | 160 |
| Water retention Gradek | 110 | 85 |
| Brightness R 457 + UV | 97.5 | 98 |
| Brightness R 457 - UV | 84.9 | 84.9 |
| WCIE | 120 | 122 |
| Gloss Tappi 75 | 70 | 70 |

Case Study 5: Removing plastic pigments in a glossy topcoat - Stiff blade - 1500m/mn - 7g/m²

### CASE 6: Replacement of clay (various GCCs, Steric Stabiliser)

A pilot coater study was then done in conjunction with a mill who was interested in removing clay from a gloss formulation. In this trial, other additional factors were also studied; the effect on rheology at low and high shear rates, whether these improvements in gloss could be seen in over a range of calendaring conditions, and carbonate types and a deeper investigation into why there was loss in optical performance. The trial was ran by applying 15 g/m² top coat onto base paper precoated with 11 g/m² on a metering size press. The coating formulations and rheological properties are given below. This showed the improvements in water retention gained from the use of the steric stabiliser. This more then compensated for the loss in water retention caused by removing the clay or using finer or more narrow psd carbonates. In addition, the reduced effect on low shear viscosity allowed an increase in solids when the steric stabiliser was used.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| GCC (90%<2µm), pph | 80 | 100 | 100 | 30 | 30 | | |
| Narrow psd GCC (75%<2µm), pph | | | | 70 | 70 | | |
| GCC (95%<2µm), pph | | | | | | 100 | 100 |
| Brazilian clay, pph | 20 | | | | | | |
| Latex, pph | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| OBA, pph | 0.48 | 0.48 | 0.48 | 0.48 | 0.48 | 0.48 | 0.48 |
| CMC, pph | 0.3 | 0.3 | | 0.3 | | 0.3 | |
| Steric stabiliser, pph | | | 0.5 | | 0.5 | | 0.5 |
| % Solids | 68 | 68.7 | 69.8 | 67.9 | 68.6 | 68.6 | 69.4 |
| Viscosity 100 rpm, mPas | 1320 | 1210 | 1080 | 1150 | 1180 | 1570 | 1320 |
| Water retention, g/m² | 121 | 146 | 97 | 175 | 111 | 140 | 113 |

Case study 6: Replacement of clay using Steric Stabiliser and other grades of carbonate

The effect of the steric stabiliser on high shear viscosity is shown in *Figure 8*. Here there is an increase in the viscosity at high shear caused by increased solids and increased addition rate of the water retention aid.

The sheets were then calendered at three different loads. This confirmed the improvement in gloss over different loads using the different carbonates. However, use of the steric stabiliser alone did not compensate for the elimination of the clay but a switch to an ultrafine carbonate and the use of the steric stabiliser did.

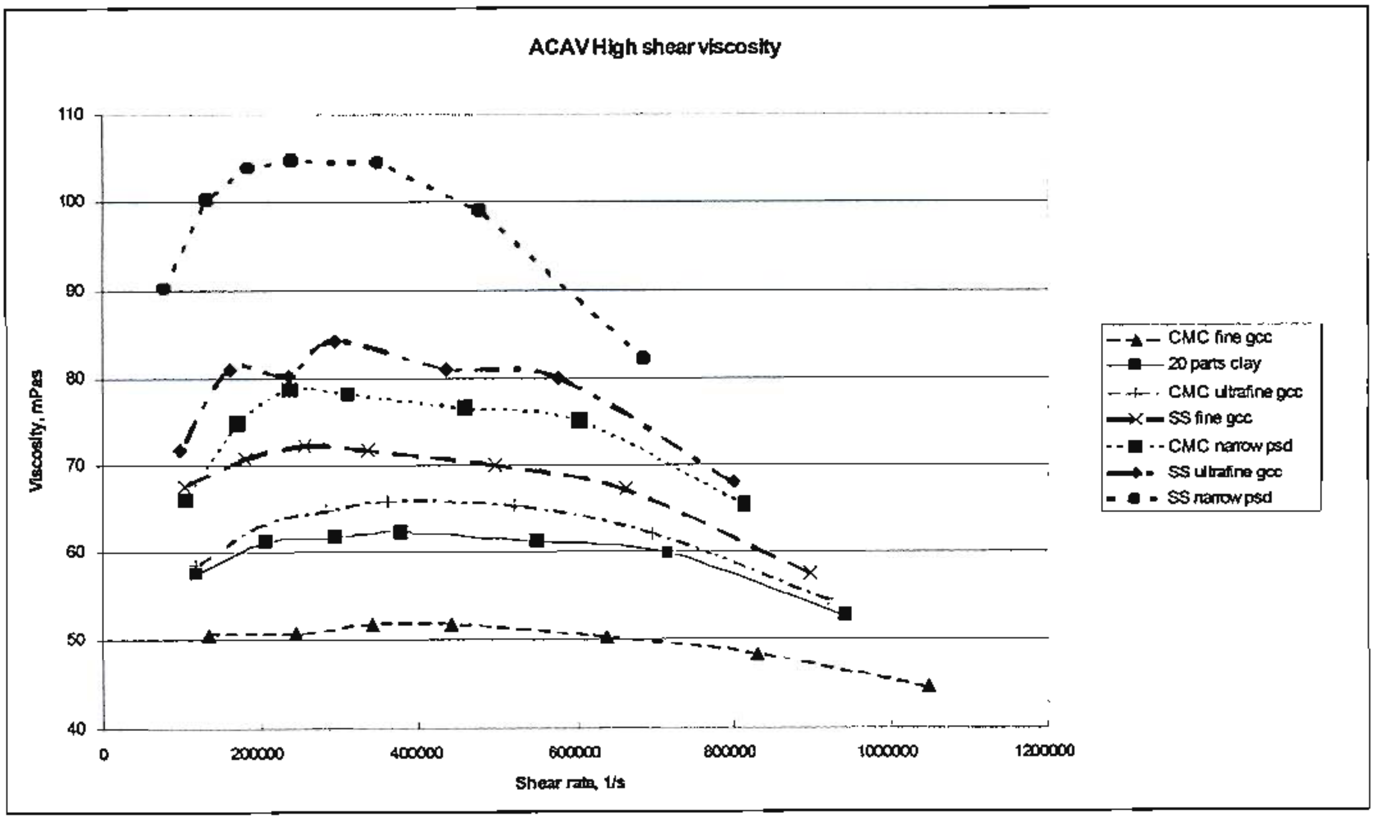

Fig.8 Effect of Steric Stabiliser on high shear viscosity

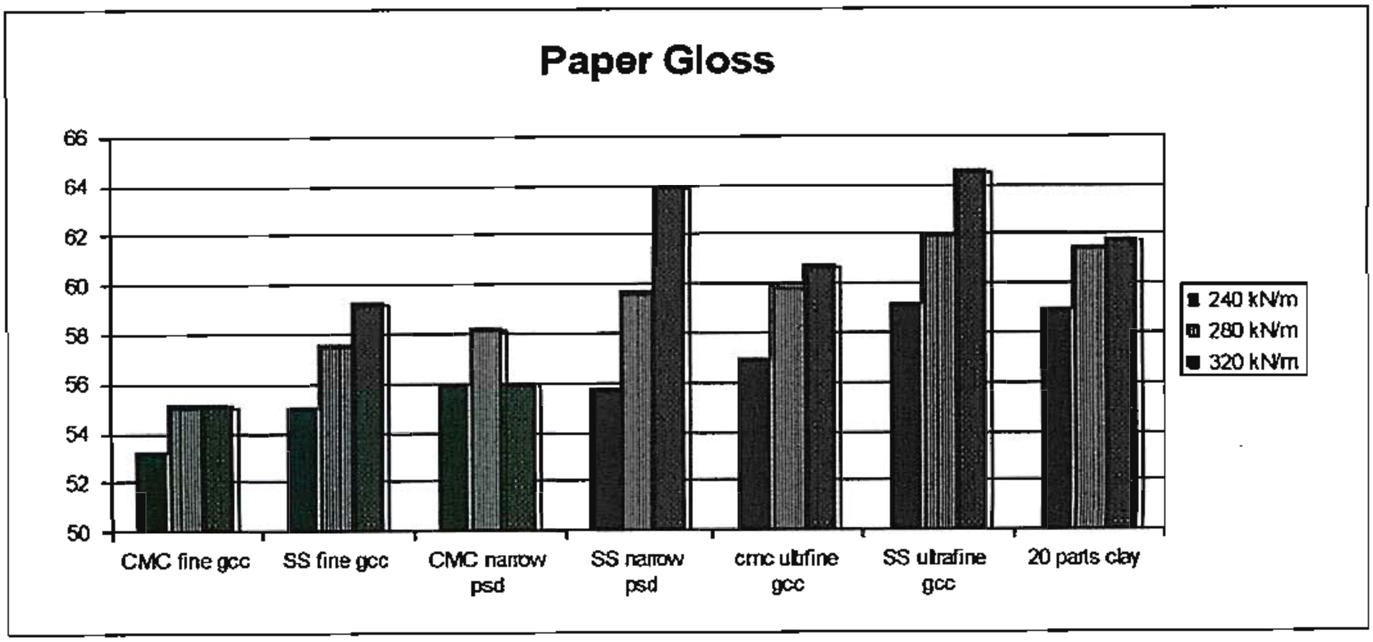

Figure 9 Effect of Steric Stabiliser on 75° gloss under a range of calendering load

Use of the steric stabiliser and removal of the clay had little effect on the Parker Print Smoothness. Indicating the changes in surface structure are small.

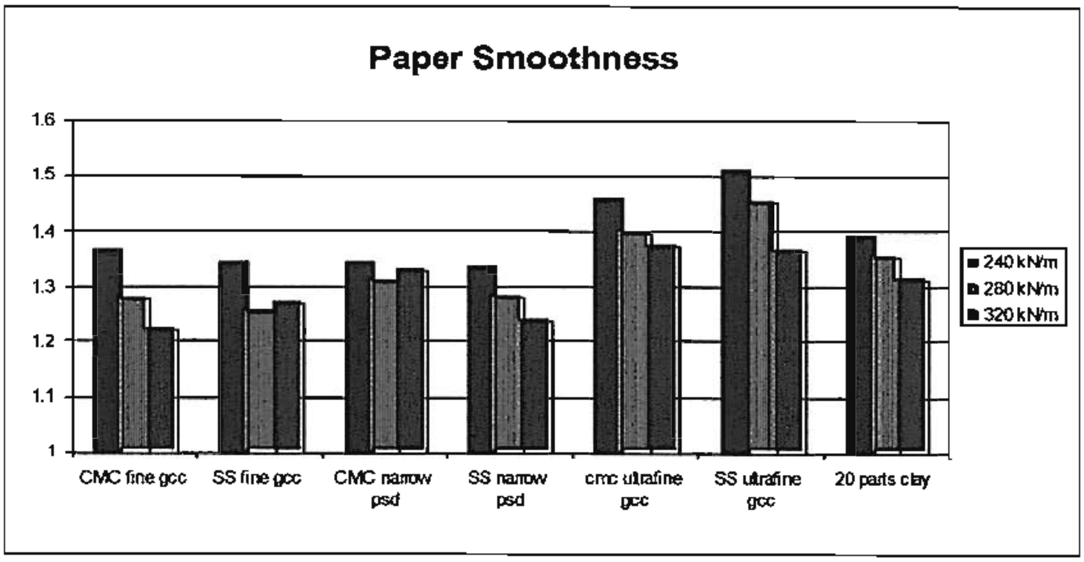

Figure 10 Effect of Steric Stabiliser on Parker Print Smoothness under a range of calendering loads

Unlike previous pilot trials, the use of the steric stabiliser did not affect the brightness with UV.

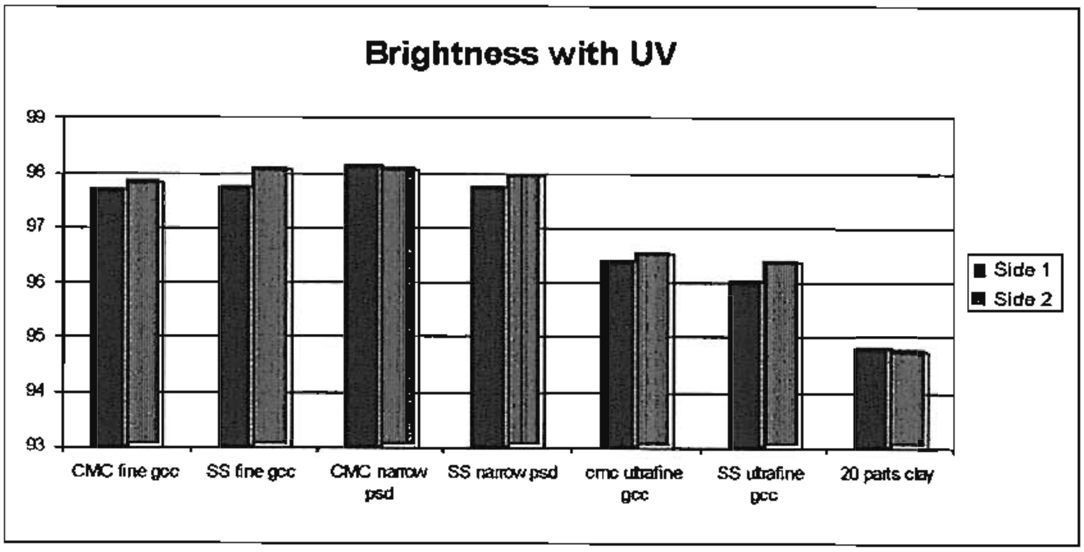

Fig 11 Effect of Steric Stabiliser on brightness with UV

This was because the steric stabiliser showed improved OBA lift over the CMC.

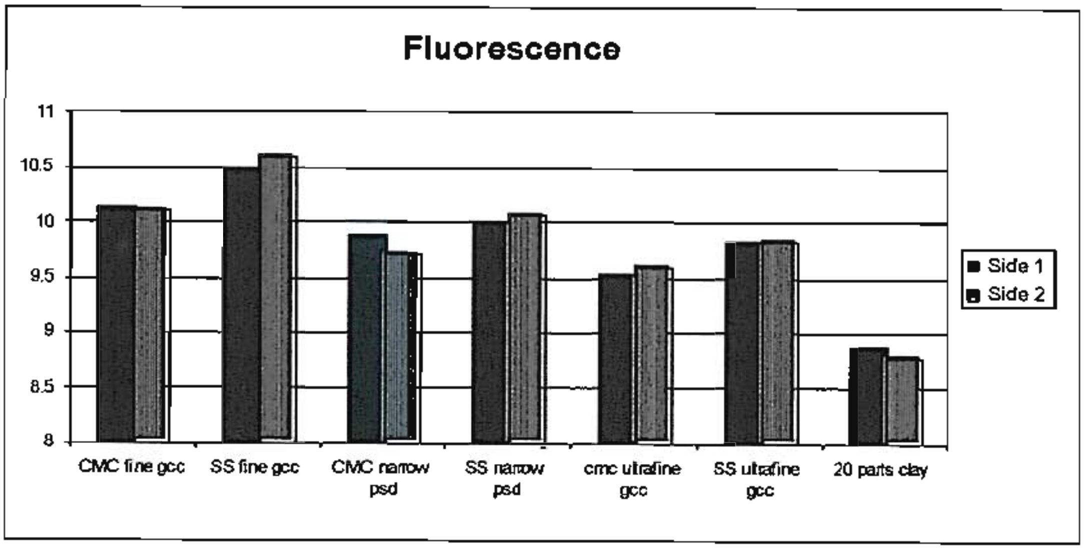

Fig 12 Effect of Steric Stabiliser on OBA lift

Therefore, use of the steric stabiliser had reduced the brightness without UV.

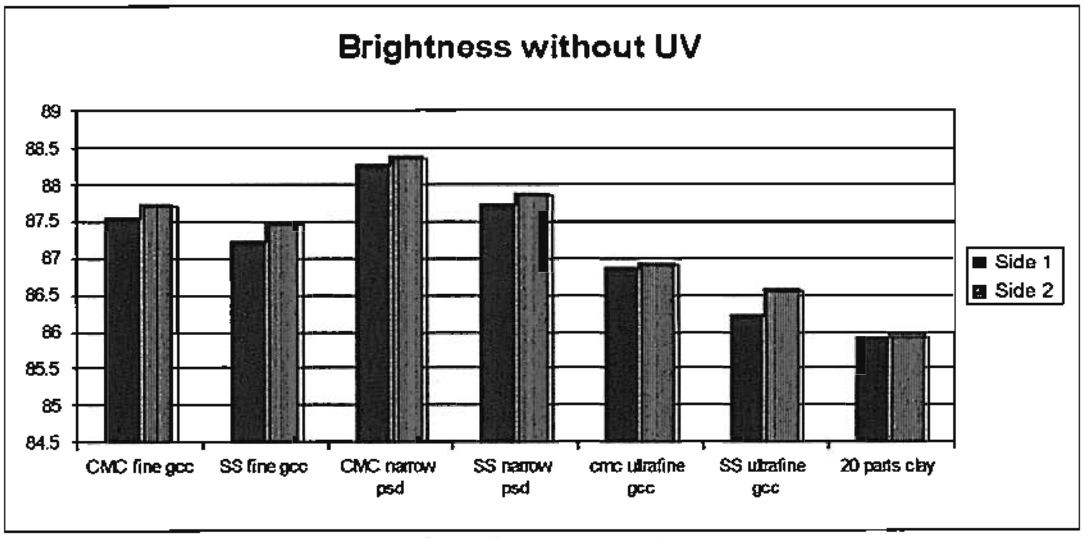

Figure 13 Effect of Steric Stabiliser on brightness without UV

This reduction arose from a decrease in the light scattering coefficient indicating a reduction in the voids in the coating as would be predicted from the mechanism.

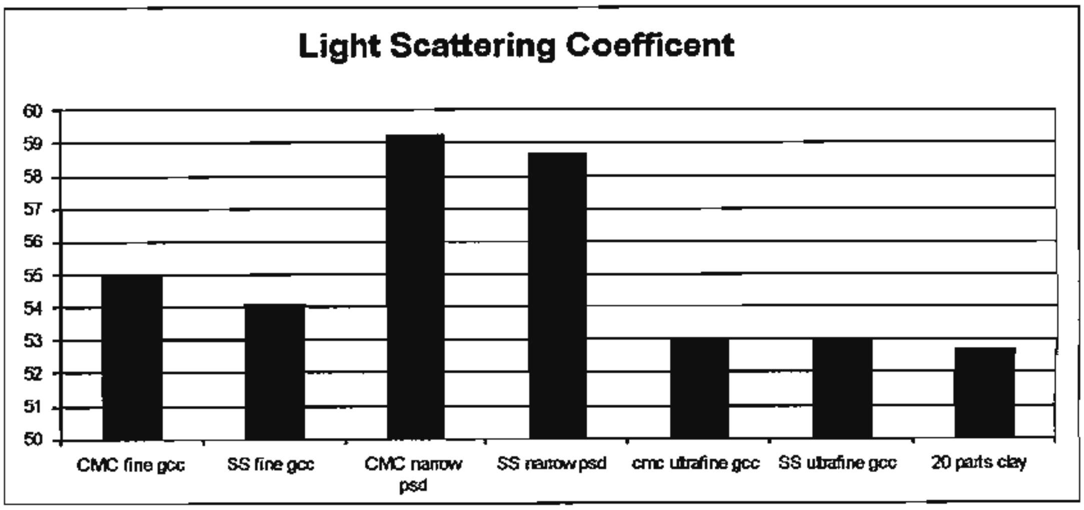

Figure 14 Effect of Steric Stabiliser on coating structure as measured by light scattering

## Conclusions

These results based on various pilot and mill trials show that by taking advantage of this new class of polymers, coating colours can be reformulated in order to improve the runnability, paper quality and cost effectiveness. The benefits of this new chemistry can be summarised as following:

- The share of carbonate can be increased
- Fine pigments can be replaced with more cost effective coarser grades
- Plastic pigment can be removed
- The solids content can be increased with excellent runnability, this leads to improved coverage and savings in drying energy
- The OBA carrying effect of the polymer and the clay replacement increase brightness

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## NOTES

# NOTES

# Titanium Dioxide and Zinc Sulphide: High-Quality Pigments for Special Papers

by
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SESSION TWO
PAPER EIGHT

## Pigments and fillers

The following provides an overview of pigments and fillers. These terms are illustrated, starting from a range of different definitions, against the background of refractive index. The whiteness of pigments and the use of optical brightening agents (OBAs) is also discussed.

## Pigment or filler? Refractive index

The definitions of the terms "pigment" and "filler" used in the paper industry differ from those of other industries that also use fine inorganic powders. In the paper industry, anything which is included in the body paper formulation in the form of an inorganic, fine-powdered material is referred to as a "filler", whereas everything which forms part of the coating is referred to as a pigment. In associated sectors, such as the paints, coatings and plastics industries, for example, differentiation is based on refractive index: All substances which have a refractive index of the order of magnitude of the binder, i.e., of the unfilled plastic (or, more precisely, "polymer") or paint resin is, traditionally, a "filler" (referred to in some of these contexts as an "extender", however) and all substances with a significantly higher refractive index are known as "pigments".

There are, without doubt, both traditional and practical reasons for these two schools of thought, but it is, nonetheless, helpful to analyze these terms in detail in order to achieve better understanding of the concept of opacity and, in particular, of wet opacity. In the case of pigments, our observation will remain restricted to the white pigments, and we will not examine the coloured pigments which are used for decorative purposes and which depend on absorption of individual wavelengths or wavelength ranges of visible light.

Both white pigments and fillers are, initially, in powder form, both white, but only white pigments retain this characteristic even after complete wetting in a system, e.g. a paint, a plastic or a "wet" label; fillers, on the other hand, become more or less transparent. This phenomenon and, therefore, the difference between pigments and fillers, is the result of differing refractive indices with respect to the surrounding medium. The following table shows a number of refractive indices for typical fillers and pigments ($N_{P/F}$). In addition, relative refractive index is also shown as the ratio of pigment/filler content to a resin system (refractive index $n_B$ = 1.48):

| | Refractive index $n_{P/F}$ | Relative refractive index |
|---|---|---|
| Blanc fixe | 1.64 | 1.11 |
| Calcium carbonate | 1.68 | 1.14 |
| Lithopone 30% | 1.86 | 1.26 |
| White lead | 1.94 | 1.31 |
| Zinc oxide | 2.03 | 1.37 |
| Zinc sulphide | 2.37 | 1.60 |
| $TiO_2$ (anatase) | 2.55 | 1.72 |
| $TiO_2$ (rutile) | 2.75 | 1.86 |

Where relative refractive index is close to 1, the system will appear transparent, whereas the more greatly relative refractive index differs from 1, the greater is scatter which, ultimately, is the factor which in the typical white pigments, zinc sulphide and titanium dioxide, ensures a white and "hiding" colouration even after complete wetting. It is also apparent that, in terms of optical properties, titanium dioxide in its rutile modification must be the most effective white pigment. Practically all commonly used binders have a refractive index of around 1.5, with the result that their influence can initially be ignored in the case of paints, coating and plastics. The situation is different in the case of paper, since only partially wetted systems occur in this field in many cases.

This dependency can be illustrated particularly strikingly using the example of a wet chalk mark on a school blackboard; as long as the chalk remains wet, i.e., present in an aqueous medium, relative refractive index is close to 1; the mark is practically invisible. As the water gradually evaporates, it is replaced as the "binder" by air, which has a significantly lower refractive index. Relative refractive index increases greatly and the chalk mark becomes visible. In formal terms, the chalk filler has become the chalk pigment as a result of changing of the medium! A further example of this dependency can be found in the white foam "head" at the top of a glass of beer; here, bubbles of carbon dioxide with an extremely low refractive index act as the pigment, embedded in ultra-fine membranes of beer which, for their part, have a higher refractive index. Relative refractive index is therefore again different from 1 and the beer foam is white (a special feature in this case is, however, the fact that the binder is the participant with the higher refractive index).

Against this background, all inorganic constituents of body paper should really be referred to as "pigments", since they are all present in the body paper to a more or less pronounced extent on the interface with the air. Practically all fillers (using the paper industry's definition) therefore exhibit "pigment" properties. The body paper is "white". If the body paper is wetted with melamine resin, for example, as in the case of decorative papers below, however, a material with a high refractive index, such as titanium dioxide, for example, must then be used in order to retain the white coloration. A material with a low refractive index, such as calcium carbonate, for example, would not achieve this.

It should be noted, for the sake of completeness, that particle size also has a significant influence on the effectiveness of a white pigment. This can be illustrated using the example of glass beads of differing sizes. The smaller the beads are, the greater the visual impression of "white". Scatter is at its optimum when particle size is approximately half of the radiation wavelength to be scattered. This signifies a particle size of 0.3 to 0.4 $\mu m$ in the case of visible light. Even smaller particles then start to become increasingly transparent. These correlations are summarized in the following approximation formula, *Figure 1*.

A further "trap" must, in detail, be added in the case of coloured papers if substances with a high refractive index are used:

In case of combination of titanium dioxide pigments with coloured pigments, the dependence on particle-size results in restrictions on selection of potential alternative pigments. The apparently easily verifiable correlation between particle-size and scattered wavelength is, in fact, made more complicated by the fact that there is no such thing as a "white" wavelength. "White" is simply the summation of all the colours of the rainbow. A particular pigment is, correspondingly, optimum only for a particular colour. Other colours are scattered less efficiently. This means, transposed to the context of coloured papers, that only a greater layer thickness will provide hiding power for these non-optimum colours; the propagation time of the ray of light in the paper is, therefore, longer. In a paper which does not contain only white pigments, this results in differing attenuation (=absorption) of individual colours. Titanium dioxide thus superimposes an additional hue on the primary colour. The result is generally more bluish or more yellowish shades of grey, for example. Corresponding titanium dioxide types are not compatible, i.e., they cannot be interchanged with one another. The tolerable "window" is of differing size, depending on requirements, and colour mixing systems usually make the greatest demands, *Figure 2*.

## Brightness and whiteness

The conditions under which a substance is capable of scattering back incident light as a result of a significant difference in refractive index vis-à-vis the medium have been examined. Incident white light thus generates the impression of a white surface by means of scatter. Scatter, however, is only one requirement for the achievement of a white surface. The complete absence of absorption is also necessary, since absorbed light cannot be scattered. Uniform absorption across all wavelengths of the visible spectrum results in a more or less

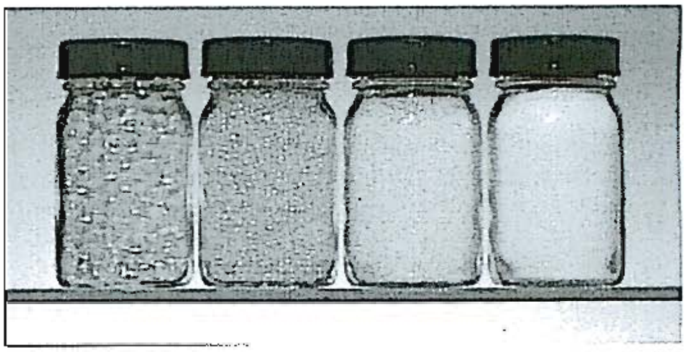
$$D = \lambda / 2.1 (n_P - n_B)$$

D: Optimum particle diameter

$\lambda$: Wavelength to be scattered

$n_P$: Refractive index of pigment

$n_B$: Refractive index of binder



Glass beads of differing sizes

Figure 1

Generation of hues via combination of titanium dioxide and carbon black. The titanium dioxide used has the best scattering power for the "yellow" wavelength. Due to the longer travel path the blue ray of light in the right-hand diagram is attenuated by the carbon black more greatly than the yellow. The overall result is thus a yellowish grey.

Figure 2

pronounced grey coloration of the surface in question, selective absorption of individual wavelengths produces a hue or a tint. Since it is generally blue light which is absorbed, the complementary colour of blue, i.e., yellow, is the colour which generally appears. Where basically white materials are used, the loss of brightness is most generally caused by impurities in the substances utilized. Natural mineral materials, in particular, nearly always contain admixtures of coloured, iron-containing (for example) silicates. Synthetic products, on the other hand, are virtually always considerably purer. Such synthetic types include, for example, PCC, Blanc fixe, titanium dioxide and zinc sulphide.

The whiteness of a paper is, ultimately, the result of the combination of the effects described; the materials used must have a high brightness, whereas possible absorption by impurities can be balanced out at least partially by the selection of a material with a high refractive index. This is true, in particular, when the entire system is totally or partially wetted. High refractive index becomes more and more important, the higher the degree of wetting. Where wetting must be anticipated during subsequent use of a paper, only materials with a high refractive index can be used if the requirement for whiteness is to be retained even under these conditions, i.e., in case of a need for wet opacity or oil opacity in label papers.

## Use of optical brightening agents

Optical brightening agents are frequently used in cases in which the brightness of a paper is not adequate or in which the production of a particularly bluish-hued paper is required. These substances are compounds which convert near UV light to visible – generally blue – light. Unlike blue pigments, which absorb the complementary colour, yellow, and thus, ultimately, achieve the required bluish hue at the cost of a loss of brightness, total brightness is not only retained but actually increased when OBAs are used.

The incorporation of OBAs, does, however, presuppose appropriate selection of the other substances used. If any one of these substances is an absorber of UV light, precisely this wavelength range will be absent for the OBA, and the use of the OBA will be pointless. Titanium dioxide, in particular, unfortunately exhibits extremely high absorption of UV light, starting more or less at the boundary between the visible and the UV range (this, for instance, is the reason for the widespread use of ultra-fine titanium dioxide in sun-blocker cosmetic products). The advantageous use of titanium dioxide (with the highest refractive index of all commonly used substances) in combination with the "bluing" properties of OBAs is therefore virtually impossible.

## The properties of titanium dioxide and zinc sulphide pigments

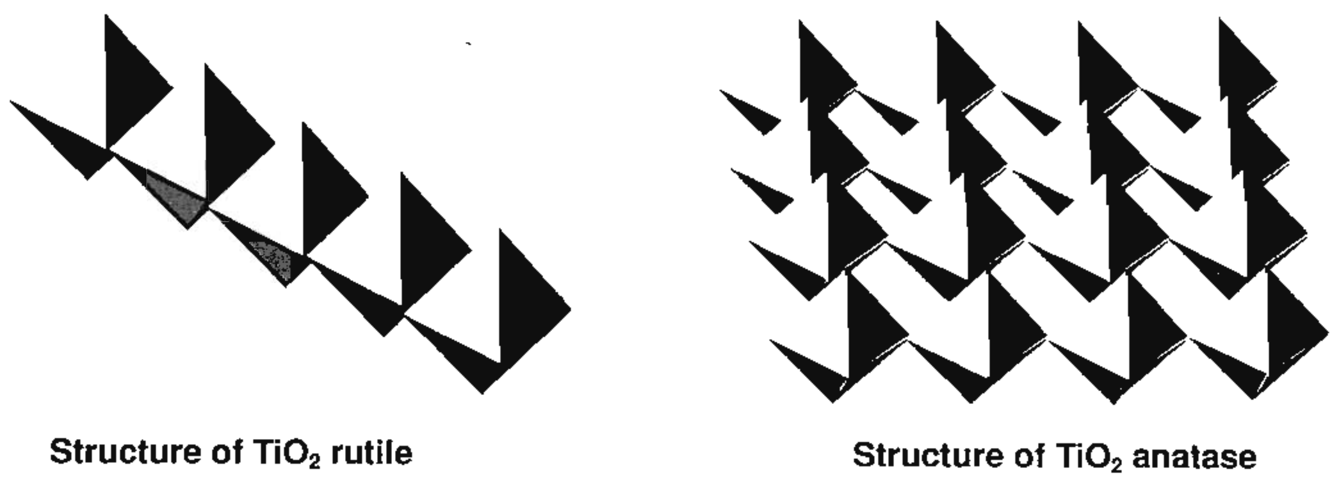
Two of the three known mineral crystal modifications of titanium dioxide, anatase and rutile, are produced synthetically on an industrial scale, while the third, Brookite, has no commercial significance:

| Rutile | Anatase |
|---|---|
| • white | • white |
| • hard | • softer |
| • resistant | • photoactive |
| • yellowish | • bluish |
| • higher specific weight | • lower specific weight |

Despite the fact that, in terms of chemical structure, both modifications consist of octahedrons with a titanium atom at the centre and one oxygen atom at each of the six corners, the differences between them can be explained in terms of the differing interlinking of these basic building elements. More corner-to-corner contacts are present in anatase than in rutile, in which edge-to-edge contacts predominate. Rutile's higher density, greater hardness, slightly higher refractive index (correlating to the optically higher density) and, probably, also lower photoactivity, are the automatic result, *Figure 3.*

As far as the light fastness of complete systems is concerned, there is scarcely any other pigment which is so ambiguous as titanium dioxide; it absorbs incident UV light completely, on the one hand, and thus protects the deeper layers of coating located in its UV "shadow" against UV-induced damage; the UV energy absorbed is, on the other hand, converted to "chemical energy": Hydroxyl radicals attack the surrounding area and destroy it oxidatively. The promoted electron leaves in the valence band a positive hole, which is extremely mobile and thus reaches the surface of the particle. Here it encounters hydroxyl ions which, in combination with it, form hydroxyl radicals, which then start their destructive work.

All titanium dioxide manufacturers counter this behaviour using two strategies; on the one hand, the crystal lattice can be doped, i.e., interspersed with small quantities of extraneous


**Structure of $TiO_2$ rutile**

**Structure of $TiO_2$ anatase**

Figure 3

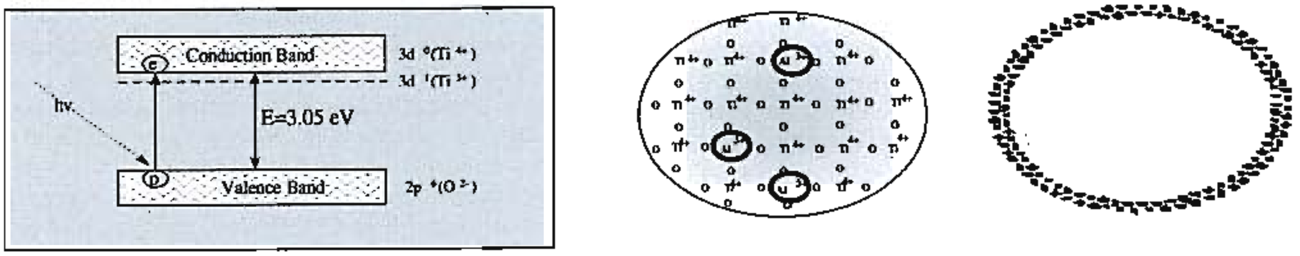
atoms in replacement for titanium atoms. This modifies the electron structure and thus the mobility of the positive holes. In addition, an inorganic coating, which prevents direct contact between the sensitive organic environment and the surface of the titanium dioxide, can be applied to the titanium dioxide particles. The protective action is clearly emphasized in correspondingly treated pigments; system stability is significantly enhanced. Unstabilized pigments, on the other hand, are deliberately used to achieve controlled "chalking", with its desirable self-cleaning effect. In this case, the binder is broken down so quickly that clean white surfaces appear again and again, *Figure 4*.

The large number of different titanium dioxide pigments available on the market becomes understandable against this background. Untreated anatase pigments are generally used in the paper industry, for cost reasons. Untreated rutile pigments may also be used if particularly high opacity is required. Inorganic coated pigments are also used in coating formulations, whereby the motivation here is less the further increased photostability compared to untreated rutile and instead the exploitation of the new interface properties resulting from the modified surface, which are generally apparent in the form of significantly greater stability of the slurries thus prepared, or in retention, however.

Unlike the familiar titanium dioxide pigments, the use of zinc sulphide pigments in the paper industry is much less widespread, despite the fact that these pigments have a considerably longer history than the titanium dioxides. The reason for this can be found in these substances' only limited stability vis-à-vis acids, which has excluded their use in case of simultaneous acidic sizing. In addition, optical performance is somewhat poorer, due to the slightly lower refractive index, without the compensation of a direct price advantage. Zinc sulphide pigments do, however, possess over titanium dioxide one decisive benefit, which can now, in times of neutral sizing, be exploited: Zinc sulphide is transparent in the wavelength range in which OBAs function. Optical brightening agents can thus be combined with a substance which has a high refractive index; in other words, wet opacity plus ultra-high whiteness. Zinc sulphide, furthermore, on the basis of the Mohs hardness scale, is an extremely soft pigment, with the result that the "Abrasion" factor does not impose any restrictions, *Figure 5*.

## Incorporation of pigments into systems

Although the same rules apply in principle to all fine-particled additives for papers and coatings, "pigments" such as titanium dioxide and zinc sulphide, for example, are the group with by far the greatest fineness. By reason of the optical



**Titanium dioxide band model** **Doping with aluminium** **Inorganic coating**

Figure 4

**The Mohs hardness scale**

**Diamond**
**Corundum**
**Topaz**
**Quartz**
**Feldspar**
**Apatite**
**Fluorite**
**Calcite**
**Gypsum**
**Talc**

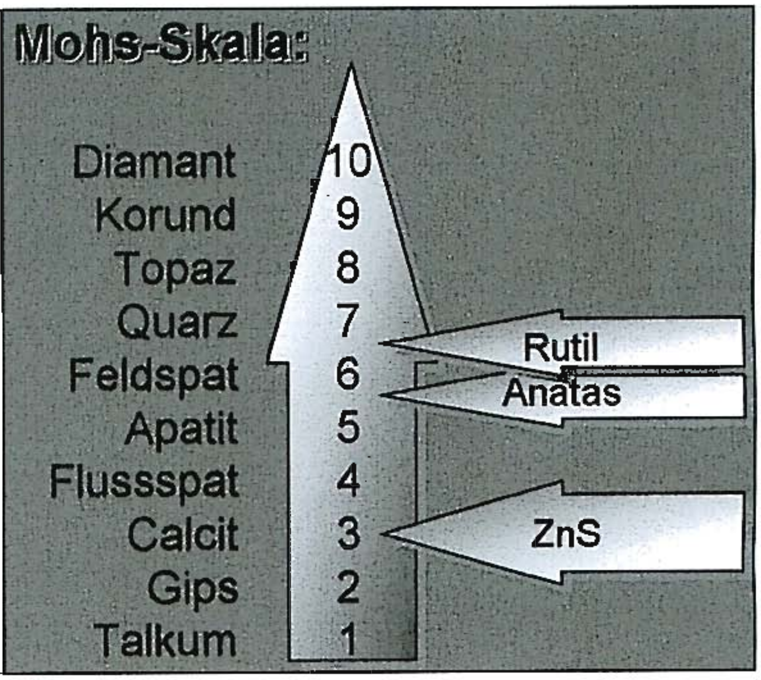


Figure 5

necessities already discussed, their size is fixed at around 300 nm. These dimensions mean that it is necessary to obey the rules of dispersion particularly strictly if the commercially available slurries, i.e., pre-dispersions, are not used.

It is generally necessary to differentiate between three operations in the incorporation of a pigment or filler; these are examined individually below. It is, firstly, helpful to study the state of the pigment as such, however. Pigments are generally powders. The elementary units of such powders are referred to as "primary" or "individual" particles. Due to their mutual contact, they accumulate to form aggregates as a result of their high mutual adhesion forces. These intermeshed aggregates form a larger unit contacting with them at their corners and edges, so-called agglomerates. The objective of incorporation must now be that of breaking down and uniformly distributing all agglomerates. Aggregates, on the other hand, can no longer be broken down during incorporation. The overall incorporation procedure is generally referred to as "dispersion".

## Wetting

The pigment to be incorporated is initially dry, i.e., all interfaces are saturated with air. This air must be replaced by the liquid phase when this pigment is now put into a liquid. This operation depends both on the geometrical preconditions of the agglomerate, on the physical and chemical interactions between the liquid and the surface of the solid and, finally, on the viscosity of the liquid. The phenomenon of "wetting" can in principle be described using the generally known Hagen-Poiseuille viscosity equation, since the liquid must penetrate into the interstices of an agglomerate (capillaries). Substitution of wetting tension which, for its part, is dependent on angle of contact and surface tension, for pressure difference, produces the known Washburn equation:

$$\frac{V}{t} = \frac{\pi \cdot R^3 \cdot \sigma_L \cdot \cos \Theta}{2 \cdot \eta \cdot l}$$

| | |
|---|---|
| $V$: | Volume of liquid transported |
| $t$: | Time |
| $R$: | Capillary radius |
| $\eta$: | Viscosity |
| $l$: | Length of capillaries |
| $\sigma_L$: | Surface tension of liquid |
| $\Theta$: | Angle of contact |

The determinant factor is therefore capillary radius, which is rated with a power of three. The more loosely the agglomerate is packed, the more easily it can also be wetted, and the greater the quantity of liquid transported per unit of time. The product of surface tension and angle of contact primarily describes the physical and chemical interaction and will vary from system to system. A large agglomerate and, therefore, a great capillary length, on the other hand, reduces wetting. Since it is contained in the denominator, a high viscosity will also have a negative effect.

It is assumed, in general, that readily mobile low-molecular-weight constituents of a liquid are firstly responsible for the initial expulsion of the air, whereas higher-molecular-weight components, such as the binder, for example, "follow up". Where capillary cross-sections are extremely small (pores), blockage may actually occur as a result of excessively large binder units. Reduction of binder concentration is generally the only recourse if such a pigment is nonetheless to be wetted. Typical wetting agents act either via modification of the surface tension, or themselves perform primary wetting.

## Dispersion

The dispersion operation involves the input of energy at least equivalent to the adhesive energy of the individual agglomerates. For any individual agglomerate, this signifies that it must, both spatially and chronologically, enter a situation in which forces of such differing magnitudes act on the two "ends" of the agglomerate that the adhesive energy is overcome. This generally occurs as a result of shearing in a velocity gradient. We should, at this point, examine in somewhat more detail that standard item of paper-industry equipment, the dissolver or toothed-disk stirrer. The greatest velocity prevails at the teeth of the disk, and declines slowly to zero toward the dissolver receptacle. Any agglomerate on this velocity gradient must therefore move more quickly on one side than on the other; it will be disintegrated (or will start to rotate). At the same time, it also becomes clear that, as from a certain agglomerate "smallness", and with otherwise identical adhesion energies, the velocity difference will become so slight that breakdown is no longer achieved. The best results are attained when the dispersion geometry as a function of dispersion disk diameter is retained, *Figure 6*.

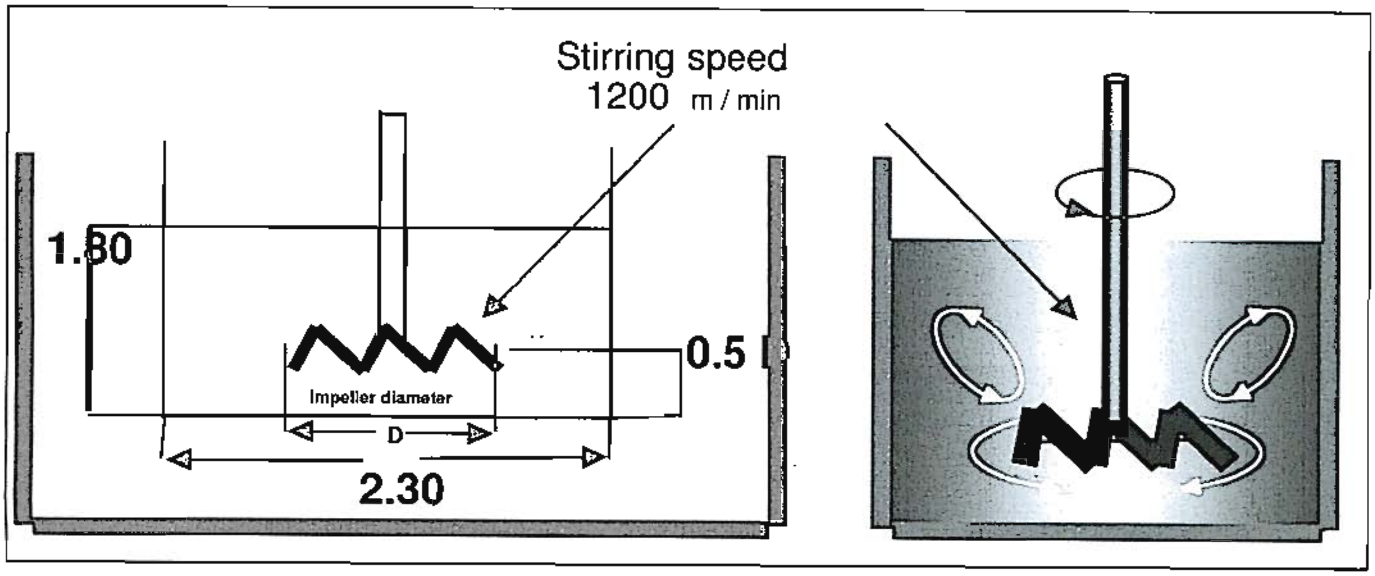


Figure 6

## Stabilization

Once breakdown of all agglomerates has been achieved during dispersion, it must be ensured during the stabilization step that re-agglomeration, or "flocculation", is excluded. Flocculation will always occur if it is easier for a system to be "flocculated" (the system, in thermodynamic terms, has a lower energy content). This can be counteracted in two different ways:

- Electrostatic stabilization
- Steric stabilization

Electrostatic stabilization is always capable of playing a role in cases in which ion pairs, which possess a different solvation potential in the system or a different adsorption capacity on the pigment surface, are present in the system. In both cases, selective absorption will occur of only one ion type, which will subsequently impress its charge on the pigment particle. Like ("same-sign") charging of all the particles in a system thus results in mutual repulsion and therefore in stabilization.

In water, salts of polyacrylic acids are also frequently used in addition. The counterions, usually alkali or ammonium ions, are generally better solvatable in water than the relatively large polyacrylic acid anion. The anion correspondingly remains on the pigment particle and imparts a negative charge to it. The reverse is the situation in solvent-containing systems; here, a small hard ion would remain on the pigment particle, while only the largest and only singly charged ions have an opportunity of being solvated at all in a predominantly non-polar environment. To this situation must be added pigments' own surfaces, which are frequently hydroxidic and thus more readily accept negative charges.

A disadvantage of electrostatic stabilization, at least in water, is the significant dependency on pH of both the ion pair and the pigment surface charge (location of the Zeta potential). A critical situation occurs when, at a selected pH, two different pigments carry unlike (+ or -) charges. Immediate flocculation would occur here.

Steric stabilization is based primarily on a simple principle: Something acts as a "spacer" between two converging particles and thus prevents further attraction and, ultimately, flocculation. Close examination indicates, however, that other effects, such as osmotic pressure in the immediate vicinity of a pigment particle, for example, also play a role. Since these mechanisms are significant in the paper industry only in exceptional cases, however, this form of stabilization will not be examined in more detail here.

## The toxicology of titanium dioxide and zinc sulphide

Neither titanium dioxide nor zinc sulphide are toxic, nor is either of them a "hazardous substance" in the sense of the German "GefStoffV" (Hazardous Substances Ordinance) and EU Hazardous Substances Directive 67/548, and they are therefore not subject to mandatory marking as such; nor is either classified as a water-pollutant. No R (Risk) or S (Safety) statements are therefore applicable. In the USA, FDA 176, under which titanium dioxide is listed as one of the "INDIRECT FOOD ADDITIVES: PAPER AND PAPERBOARD COMPONENTS", applies, and in particular Articles 176.170 (Aqueous and Fatty Food) and 176.180 (Dry Food). The requirements of CONEG, HAPS, EN 71/3 and AP(89)1 are also met. The German Tabak VO (Tobacco Ordinance) requires the use of grades which conform with the requirements for an E 171 foods additive, but such grades are available. It is possible here, due to the large number of regulations applicable around the world, to state only those with a certain general applicability, but a large range of other lists also exists and must be checked jointly with the manufacturer in each individual case.

## "Pigment" and paper

As already discussed, the use of substances possessing a high refractive index permits the production of papers with good wet opacity and also whiteness; the individual products do, however, possess in detail significantly differing effects on the other optical parameters.

## Opacity and whiteness

Whiteness has already been defined as a combination of powder brightness and opacity. The differences between the individual product groups, i.e., rutile, anatase and zinc sulphide, become clearly apparent when opacity is plotted against

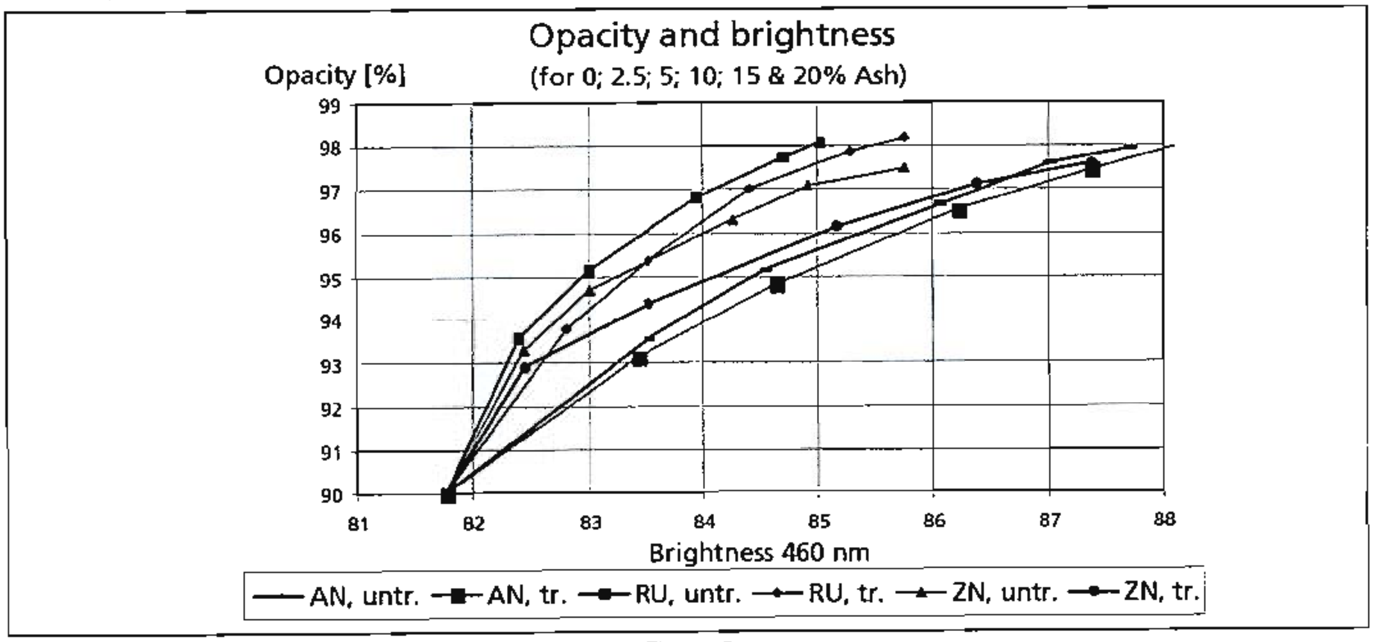


Figure 7

the achieved brightness. Any inorganic coating possibly present has a significantly lower effect in this view, on the other hand.

Rutile (due to its having the highest refractive index) thus has the highest opacity, followed by zinc sulphide and anatase. Despite their somewhat lower opacity, higher brightnesses can be achieved with zinc sulphide or anatase, however, if the R46 is observed. The slightly less blue L* value reacts slightly less to the differences.

## Colour location

With respect to the colour location achievable or occurring, the differences are more fundamental than in the cases of opacity and whiteness. While anatase causes a shift into the blue/red range, the use of zinc sulphide results in a blue/green shift. In this case, the coating has a comparatively great influence, but it must be remembered that this material is not a commercial product. Rutile also drifts slightly toward red, but the drift is not unequivocal on the blue/yellow axis:

## Combination with optical brightening agents

OBAs require exploitable ultra-violet light to permit their unimpaired functioning. The simultaneous use of UV-absorbing substances is therefore counterproductive. In the graphic below, the "pigment-free" paper coating, which contains "only" calcium carbonate, exhibits in measurement of R 460 nm brightness the greatest increase in brightness in white upon addition of UV light. Opacity, measured as R 460 nm brightness on a black background is, however, modest and is improved only insignificantly by UV light. Partial replacement of calcium carbonate with rutile immediately indicates the dramatically superior concealing of the background, but the addition of UV light increases brightness over white only marginally. Zinc sulphide also exhibits significantly improved hiding power over a black background, but additional UV light also results additionally in a significant increase in brightness over white. If all other boundary conditions are also correct, this example demonstrates how high brightness can be combined with good opacity. The graphic should, in this context, be understood as follows: A point occupies the X/Y coordinates of R460 measurement of diffuse reflectance against black and white, in each case. The two points at which measurements of diffuse reflectance were performed with and without UV light components are connected in each case, *Figure 9*.

## Specimen applications for "pigments"

By definition, pigments with a high refractive index are always used where papers are to remain opaque despite being (temporarily) wetted, as in the case, for example, of label papers (wet and oil opacity) and when a dark background is to be permanently concealed. This may apply, for example, to a paper coating on body paper with a recycled-paper content. Here, the low body paper price must be set against the higher price for pigments. It is necessary, of course, to also take more far-reaching effects into account to achieve a complete calculation, since not only the darker colour of recycled paper but also, for example, more heavily coloured and therefore generally cheaper additives can be balanced against the more expensive pigments, with a system formulation price which

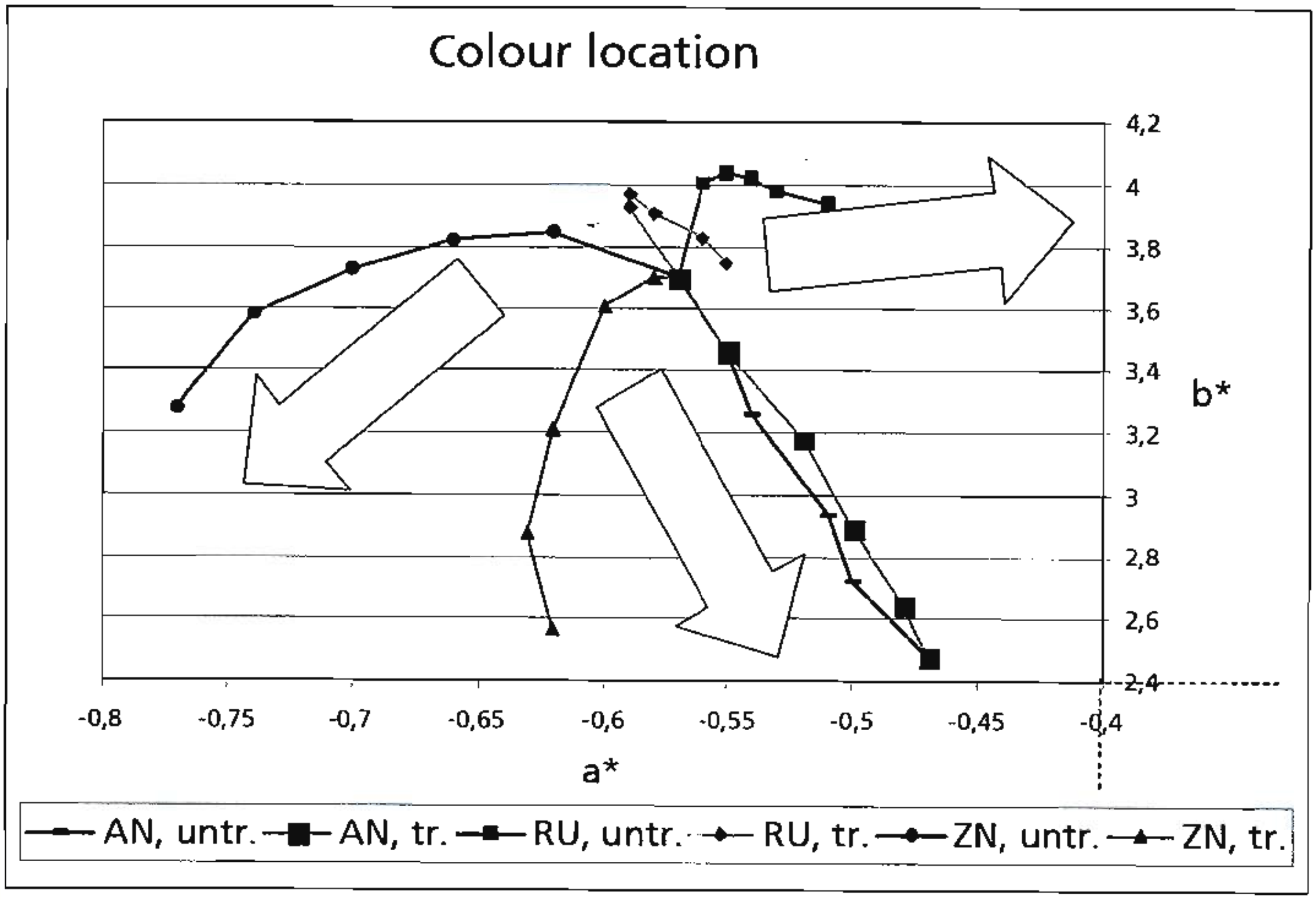


Figure 8

will provide a decision-making basis as the result. The same applies to the use of OBAs, which harmonize well with zinc-sulphide pigments and can thus be used at lower concentrations.

The calculation must include not only purely raw materials prices, but also continuous operating costs. Rapid dispersion, good drying properties thanks to low specific surface and long machine-component service-lives achieved via the use of soft pigments for embossed papers, as in certain wallpapers, for example, thus also assist in optimizing costs.

Experience indicates, all in all, that each and every individual case must also be examined individually; there are (unfortunately) only very few universally applicable system rules which can be used for the precise definition of optimum use of pigments, selection of types and grades, and best delivery form.

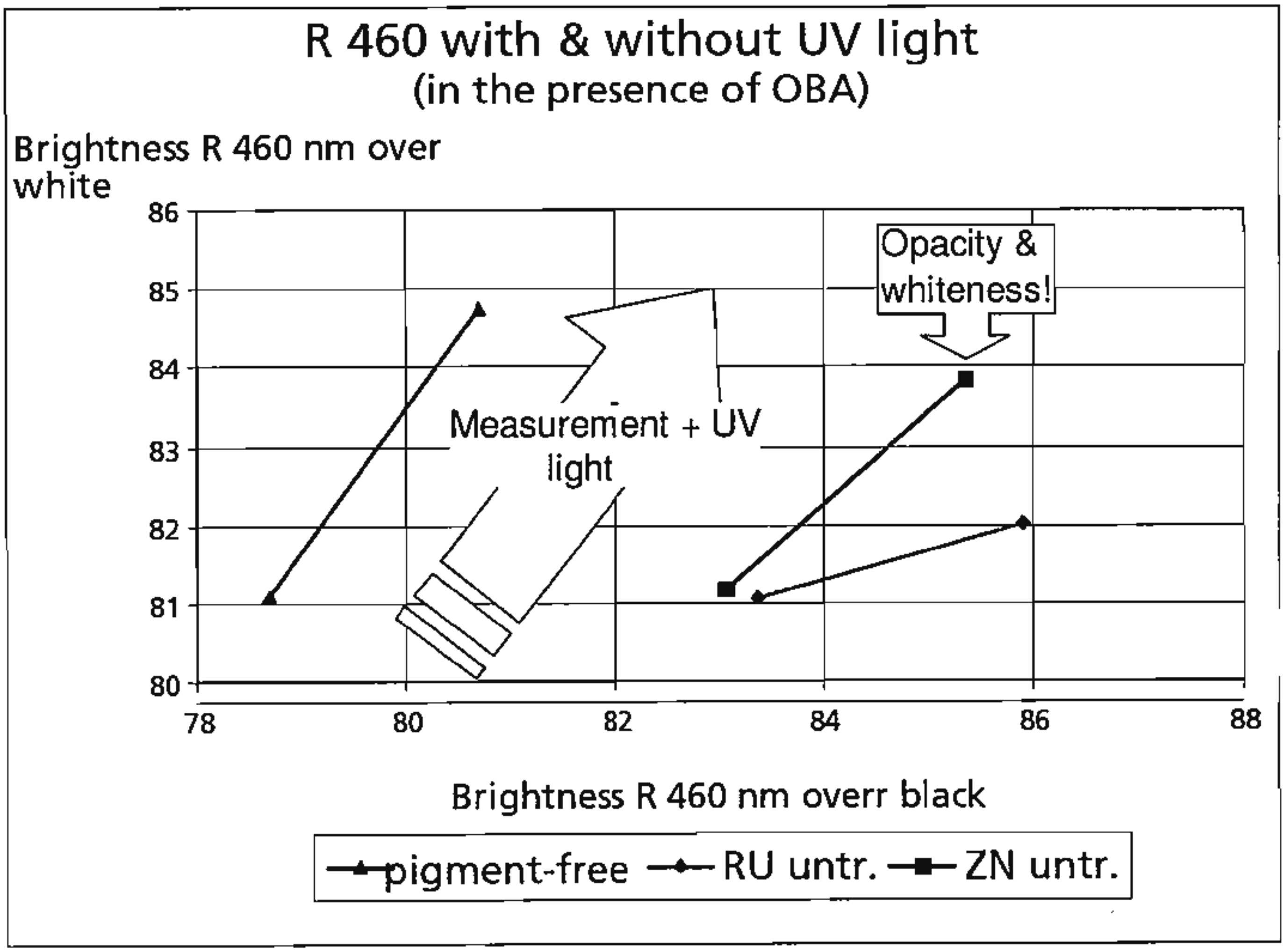


Figure 9

# Replacement of Latex by Natural Polymer Binders in Coating

by
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SESSION TWO
PAPER NINE

## Summary

The coating of papers is an important step in determining the final quality of the product. The coating recipe has an influence on the optical and physical characteristics of the sheet as well as the printability. Given the high cost and non-biodegradable nature of synthetic latices derived from oil, an interesting alternative is the use of natural polymers made from renewable resources. *Roquette*, a manufacturer of starch and starch derivatives for the paper, food and pharmaceutical industries have developed a range of binders specifically for paper coating. These natural polymer binders are optimised to obtain a stable, high solids glues. The replacement of synthetic latex is possible without loss in coating solids. Coating colours containing these natural binders have a rheological behaviour adapted to suit all types of coating and give excellent offset printing properties. In addition, compared to oxidised starches sometimes used in pigment coating and which have an anionic charge, these natural polymer binders are non-ionic and result in a lower COD and better fixation of cationic additives during the re-cycling of the broke.

**Key words:** natural polymer binders - coating recipes - pre-coat - top-coat -offset printability

## Introduction

The qualities looked for in a coated sheet include: brightness, opacity, gloss smoothness, and printability. During offset printing, the paper should allow faithful image reproduction with a good printing gloss gain, to improve reading comfort, and a homogeneous reproduction of the solid colour areas (no mottling).

To obtain the desired final sheet qualities, the papermaker can modify:

- The base sheet properties: fibre composition, additives, porosity, absorption capacity, formation.....
- The coating colour recipe and its characteristics: pigments, binder and co-binders, additives, coating solids, water retention....
- The type of coater
- The drying of the base paper and the coatings. The most widely used technique for drying coatings is the High-Low-High strategy to avoid binder migration[1-5].

Roquette have developed a range of thermally modified natural polymer binders marketed under the name *Stabilys®*. These binders can be used in both pre-coat and top-coat recipes. This allows the coating cost to be reduced by partial or total replacement of synthetic latices while maintaining the final paper quality. In our Application Laboratories in Lestrem we have two pilot coaters for small-scale production of coated papers. We have studied more specifically the influence of the composition of the coating colour (binder ratio, proportion and type of binders and co-binders) in pre coat and top coat formulations, on the offset printability of coated papers and boards using our Dixon pilot coater and Helicoater high speed coater.

## Trial Descriptions

### Dixon Coater Trials – Binder Selection and Preparation

The Dixon Coater allows us to surface-treat or coat papers from 30-300 $g/m^{-2}$ up to a maximum speed of 150 m/min. We have a selection of coating heads enabling us to carry out trials with: size-press, film-press, blade coating, air-knife coating, Champion coating, and rod applicator. The paper, after coating, enters two-zone hot air dryer (max. temperature 200°C), an infra-red pre-dryer is also available. After drying the paper is passed over two cooling cylinders before re-winding.

For these trials the base-paper used was a 39 $g/m^{-2}$ sheet containing re-cycled fibre with a relatively high Cobb value ($Cobb_{60}$ = 50 $g/m^{-2}$). The drying temperature was fixed at 110°C.

The Stabilys® range of thermally modified natural polymer binders being developed by Roquette for paper coating is under active development. For the trials on the Dixon coater, two products from the Stabilys® range were selected together with an oxidised starch marketed for use in coating (referred to as Starch A in the result tables). These binders were used in combination with styrene butadiene latex. The recipes are given in *Table 2 (overleaf)*.

The products from chosen from the Stabilys® range and Starch A were prepared by jet cooking (3' @ 145°C) to produce a 35% solids glue. The Brookfield viscosities of the glues is given in *Table 1 (overleaf)*.

You will note that the viscosity depends both on the type of modification and the molecular weight. For the same type of modification the Brookfield viscosity is directly proportional to the molecular weight.

Stabilys® A030, the product with the lower molecular weight has a higher sol/gel transition temperature than Stabilys® A020 but the gel structure is weak and does not change the rheological behaviour of the resulting coating colour significantly.

### Analysis of the Coated Papers and Evaluation of Offset Printing Quality

After coating the papers were calendered using a Ramisch sheet calender, 1 pass at 90°C, pressure 3 bar.

The optical characteristics, surface properties and strength of the papers were measured. The tests included:

- Brightness, opacity and gloss.
- Bendtsen smoothness and porosity
- Stiffness and breaking length
- Wet and dry IGT
- One minute Cobb
- Paper surface energy, this factor is very important in order to predict the ink/paper compatibility. Offset printing inks are oil-based and it is therefore preferable to have a hydrophobic surface.

The printability of the papers was determined with the collaboration of the Centre Technique du Papier (CTP) at Douai after commercial printing on a Heidelberg SM 52 press, 4 colours (black - cyan - magenta - yellow) speed: 4400 sheets/hour. The inks used were from the Lotus+ range supplied by Coatex Lorilleux.

The following criteria were analysed:

- Optical density
- Dot gain
- Printing gloss and printing gloss gain
- trapping
- mottle
- Ink transfer and speed of ink immobilisation.
- Resistance to scuffing, see-through, debris, blistering (heat set -offset)

For commercial printing a significant quantity of paper is required, at least 500 sheets. In the laboratory, with the use of the IGT-AIC2-5 print tester and the same industrial inks, it is possible evaluate certain criteria, including some of those given above, with a more limited quantity of paper.

### Formulations for LWC Top Coat Coating Colours Based on Clay and a Clay/Calcium Carbonate Blend for Trials on the Dixon Coater

The recipes of the coating colours are given below in *Table* 2. The coating colours were tested using:

- BROOKFIELD Viscometer
- AR 2000 Rheometer (viscoelasticity and yield point)
- HERCULES Viscometer (to 40 000 $s^{-1}$)
- ACAV Viscometer (to 1 000 000$s^{-1}$)
- WARREN tester, for water retention

For formula A we replaced 7 parts of latex by 9 parts of Stabilys or Starch A, the pH was not corrected. The coating solids was 52% and the coatings were applied using the trailing blade head at 50 m/min, the blade angles (± and ≤) were set at 35° and 0° respectively to give a single-sided coat weight of 5.5 g/m$^{-2}$.

A customer recipe was used as the base for formula B, which contained a high proportion of calcium carbonate together with a lubricant, insolubiliser and dispersant. The pH was adjusted to 9, coating solids was 62.5% and 4.5 parts of latex were replaced by 5 parts of Stabilys or Starch A, leaving the binder ratio virtually unchanged. the coatings were applied using the trailing blade head at 30 m/min, the blade angles (± and ≤) were set at 20° and 0-5° respectively to give a single-sided coat weight of 13 g/m$^{-2}$.

**Comment:** It is known that a change in coat weight can influence the degree of mottling[6]. During our trials the coat weight variability was limited to 5%.

| Products | BROOKFIELD Viscosity (mPa.s) | Mean molecular weight (105 Da) | Sol/gel transition temperature* (°C) |
|---|---|---|---|
| Stabilys® A030 | 130 | 1.5 | 62 |
| Amidon A | 200 | 7 | - |
| Stabilys® A020 | 310 | 7.9 | 50 |
| **Measured by dynamic rheological analysis during the cooling of the glue.* | | | |

Table 1: Brookfield Viscosity @ 60°C, 35%MS

| | Formula A | | | Formula B | |
|---|---|---|---|---|---|
| | Reference | Trial | | Reference | Trial |
| Products | Parts | Parts | Products | Parts | Parts |
| Clay | 85 | 85 | Calcium Carbonate | 60 | 60 |
| Calcined Clay | 15 | 15 | Clay | 40 | 40 |
| Latex (SBR) | 14 | 7 | Latex (SBR) | 12.5 | 8 |
| STABILYS® or Starch A | 0 | 9 | STABILYS® or Starch A | 0 | 5 |
| CMC | 0.7 | 0.7 | CMC | 0.5 | 0.5 |
| | | | Dispersant | 0.06 | 0.06 |
| | | | Insolubiliser | 0.5 | 0.5 |
| | | | Lubricant | 0.4 | 0.4 |
| Characteristics | pH as is, 52%MS | | Characteristics | pH = 9, 62.5%MS | |

Table 2: Recipes

**High Speed Helicoater Trials**

We have used the Helicoater to carry out pre-coat and top-coat trials on both paper and board.

**Coat Trial – Board**

The coating was carried out in two stages:

- Blade application of pre-coat at 900m/min., coat-weight 10-12 g/m$^{-2}$ (single sided). The reference formula used 14 parts of latex, 0.1 parts of CMC and 0.6 parts of a synthetic thickener. Five parts of latex were replaced by STABILYS® A020. The parts of CMC and synthetic thickener were also altered to optimise the formula. The final coating solids were 63.5% and the coat weight 10-12 g/m$^{-2}$ (single-side).
- The top-coat was also applied by trailing blade at 900 m/min, coat weight 10-12 g/m$^{-2}$. The coating colour solids were 62% (o.d.).

The papers were then calendered under the same conditions as before.

**Top-coat Trials, Offset Printing**

These trials were carried out on a pre-coated wood-free base paper. The coating was applied using the trailing-blade head, the coat weights were: 10 g/m$^{-2}$ (series A) and 12 g/m$^{-2}$ (series B). The formulation of the coating colours and paper characteristics are summarised in *Tables 3 & 4 below*.

The series A papers were subsequently calendered (ABK calender, 80°C, 1st pass at 180 kN/m, 2nd pass at 130 kN/m).

The series B papers were not calendered (matt finished). The offset printing quality was evaluated by CTP (see above for conditions).

|  | Series A |  | Series B |
|---|---|---|---|
| Grammage (g/m²) | 65 | Grammage (g/m²) | 100 |
| Coat weight (g/m²) | 10 | Coat weight (g/m²) | 10 |
| Latex/starch (parts) | 4/6 | Latex/starch (parts) | 0/22 |
| Cobb 60 (g/m²) | - | Cobb 60 (g/m²) | 80 |

Table 3: Pre-coated base characteristics

**High-speed Pilot Trials**

This trial was carried out on a high speed semi-industrial pilot coater. The base paper was a 58 g/m$^{-2}$ wood-free sheet. The coating was carried out in two stages.

- A blade-applied pre-coat at 1250 m/min, 10 g/m$^{-2}$/ side. The reference formula contained 8 parts of starch, this was replaced by Stabilys® A030. The coating colour solids were 67-68%.
- The top coat was also applied by trailing blade at 1250 m/min, the coat weight was 10 g/m$^{-2}$/ side. The reference formula used latex only for the binder, the colour solids being 66-67%.

The papers were subsequently calendered.

## Results and Comments

**Dixon Trials, Formula A**

The colours were all shear thinning *(Figure 1)* and elastic. The flow viscosities of the coating colours using natural polymer binders were higher than that of the 100% latex binder reference, principally at low-shear. At high shear rates, the viscosity of all the formulas is very close. The minimum force required to induce flow was no higher for the coating colours using natural polymer than for the reference formula. The coating conditions on the machine should not therefore need to be altered.

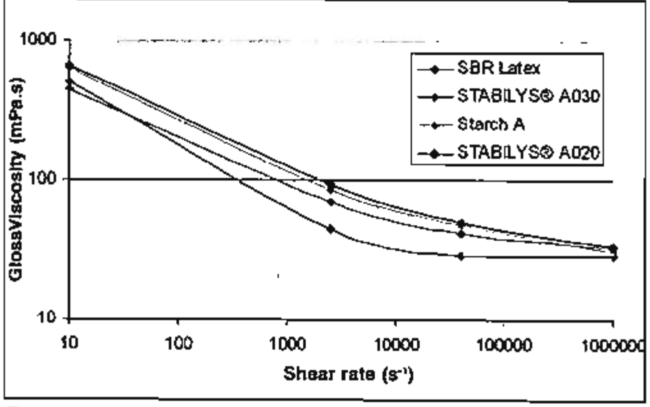

Figure 1: Viscosity of formula A colours at various shear rates

|  | Series A |  |  | Series B |  |
|---|---|---|---|---|---|
|  | Reference | Trial |  | Reference | Trial |
| Products | Parts | Parts | Products | Parts | Parts |
| Carbonate | 90 | 90 | Carbonate | 90 | 90 |
| Clay | 10 | 10 | Clay | 10 | 10 |
| Latex SBR | 10 | 8 | Latex SBR | 10 | 7 or 8 |
| STABILYS® A030 | 0 | 2 or 3 | STABILYS® A030 | 0 | 5 or 3 |
| CMC | 0.3 | 0.3 | CMC | 0.8 | 0.8 |
| OBA | 0.4 | 0.4 | PVA | 0.5 | 0.5 |
|  |  |  | OBA | 0.45 | 0.45 |
|  |  |  | Lubricant | 0.1 | 0.1 |
| Characteristics | pH = 9, 68.5%MS |  | Characteristics | pH = 9, 67%MS |  |

Table 4: Recipes

The water retention, as measured by the Warren test, was superior with colours containing natural binders. Stabilys® A030 gave a water retention of 185s, Stabilys® A020, 200s and Starch A, 175s. The reference, containing only latex, had a water retention of 120s.

Statistical analysis of the most important parameters allowed us to find a correlation between the molecular weight of the natural polymer and the water retention of the final coating colour: the lower the molecular weight, the higher the water retention. This is a result of the presence of a higher number of hydroxyl groups available to form hydrogen bonds with the water molecules.

How do the paper properties vary as a function of type of natural polymer binder used and the number of parts of binder?

The LWC papers were very similar in terms of brightness, opacity, breaking length and 60 second Cobb. Slight differences were observed in gloss and stiffness. *(Figure 2)*, the papers using natural binders in the coating were stiffer. The natural binders appear to be more resistant to calendering and this would explain the differences in gloss values, an alteration of the calendering conditions or an increase in the coating solids should enable the same levels of gloss to be achieved. After printing we have noted that the print glosses are equivalent and that the gain in print gloss was higher for the coatings containing natural polymer binders, the best results were obtained with the Stabilys® A020 *(Figure 3)*.

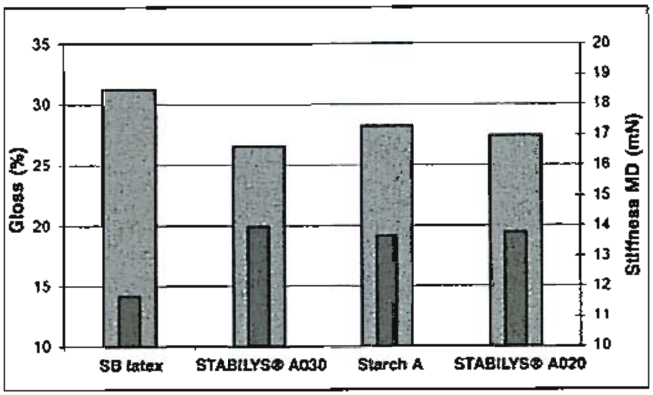

Figure 2 : Gloss and stiffness before printing

The surface strength of coated papers is very important. If the surface strength is too low, picking will occur during printing because of the tack of the inks. Generally it is felt that it is necessary to use 1½ to 2 parts of natural polymer binder to replace 1 part of latex. However it is shown in *Figure 3a* that the replacement of 7 parts of latex by 9 parts of Stabilys® gives no loss in pick strength and, in fact, the papers containing natural polymer binders give slightly higher results. In parallel the analysis of the surface energy shows that the papers containing natural polymers are more hydrophobic than the reference. We think that this is because more of the latex stays on the surface thanks to the presence of the hydrophilic natural polymer which penetrates more in to the body of the sheet.

With regard to post print mottle, the coating containing natural polymers give the same results as the 100% latex reference *(Figure 4)*. The paper containing Stabilys® A020 has a mottling index of 2.2 compared to 2.4 for the reference paper, a difference sufficient for an expert eye to see. A mottling index higher than 2.2 is regarded as poor.

Print-dot gain is also lower for the coatings containing natural polymer *(Figure 5)*.

For the other printing parameters examined, no differences between the papers were apparent.

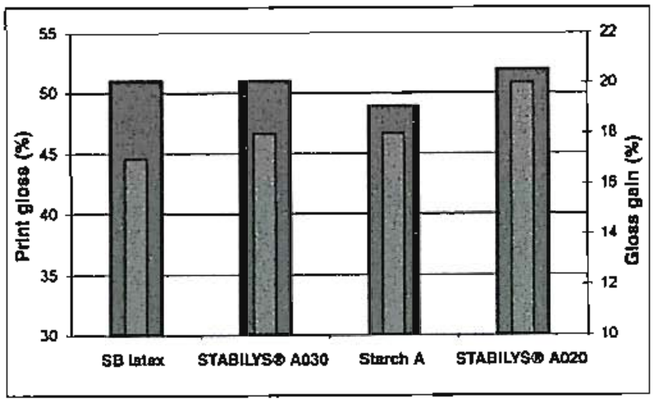

Figure 3 : Print gloss and print gloss gain

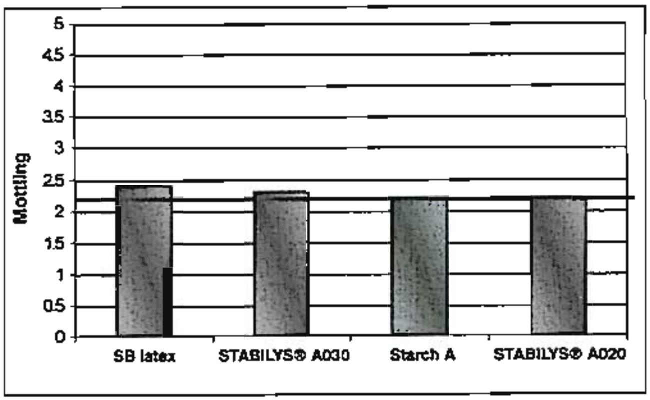

Figure 4 : Post print Mottling Index

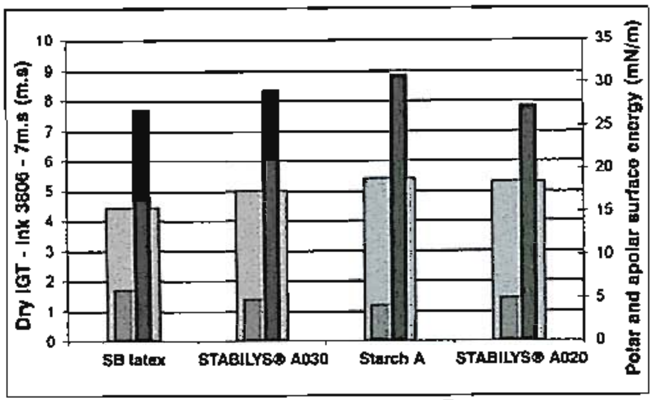

Figure 3a IGT and Surface Energy

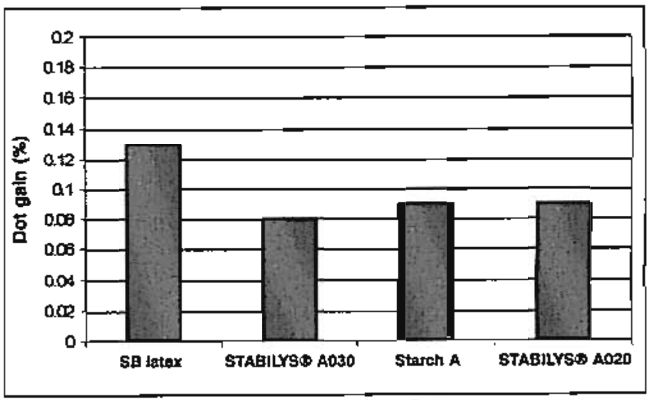

Figure 5 : Print Dot Gain

**Dixon Trials, Formula B**

All the coating colours were shear-thinning and elastic. The latex reference coating colour had the lowest viscosity across the shear range. At one million s-1, the colour containing Stabilys® A030 had a viscosity of 53 mPa.s, the colour with starch A, 52 mPa.s, Stabilys® A020, 57 mPa.s and the reference, 38 mPa.s. The viscosity level of the natural polymer containing coating colours is dependent on the type of chemical modification of the base material, the molecular weight and the interaction of the polymer with the other colour components. In all cases the differences between the four colours is relatively small and it should not be necessary to change the machine parameters for high-speed coating.

The water retention values of the coating colours containing natural polymer-based binders, as in the previous formulas, are proportional to the molecular weight of the product used. Not all the results treated in the statistical analysis allowing us to demonstrate the correlation are included in *Figure 6.*

There were some differences found in the finished papers. The paper coated with the reference formulation had the highest gloss level; of the others, the coating containing Stabilys® A020 was closest to the reference value. The coatings with natural polymer binders gave a stiffer final sheet and the print gloss and print gloss gain were higher than the reference *(Figure 7)*. The coating containing Stabilys® A030 gave the best print gloss value and gain.

The pick resistance of the coating containing Stabilys® A030 is improved compared with the reference coating. Stabilys® 030 has the lowest molecular weight of the natural polymer binders examined in the study and therefore can penetrate more easily into the base paper, the latex staying more on the surface. The loss in pick resistance of the other coatings is relatively small given that the test conditions were particularly severe (a high-tack ink was used at the maximum speed range).

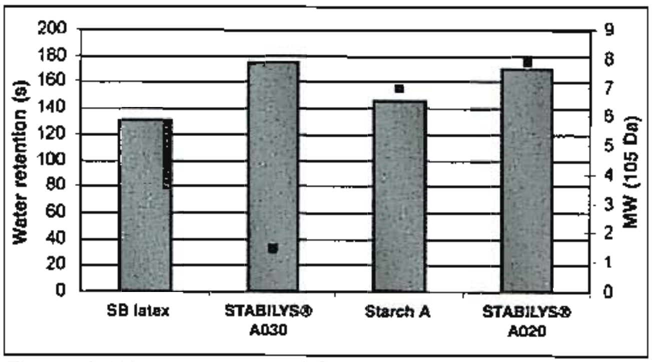

Figure 6: Water retention of Coating Colours (Warren Test) and molecular weight of the natural polymer binders

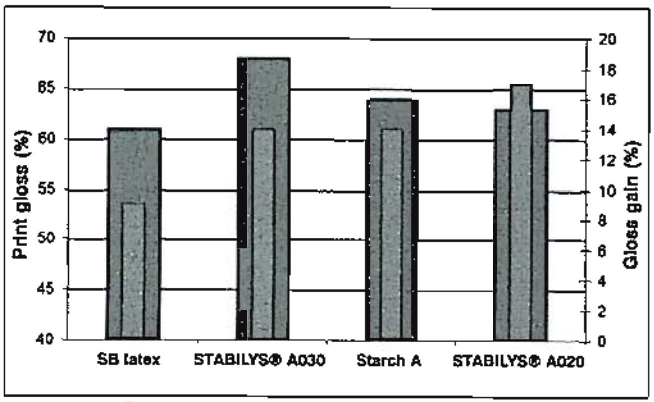

Figure 7: Print Gloss and Gloss Gain.

The papers coated with the natural polymer containing colours were more hydrophobic than the reference paper; the dispersive component was little changed but the polar component fell by around 25%. There was no significant difference between the papers treated with the three trial coatings.

The lowest mottling index was observed for the reference sheet, 2.1, then the papers containing Stabilys®, 2.3 and then Starch A, 2.4. The two extremes are discernable by an expert eye *(Figure 9)*.

We also noted that the ink transfer was faster for the papers containing Stabilys® than for the reference. The paper containing Starch A had a different ink immobilisation speed than the reference. The two types of natural polymers used in this study gave different distinguishing criteria. The distribution of the binder in the coating layer is a function of the different physio-chemical modifications of the polymer.

The other printing parameters examined showed no differences between the papers.

**Helicoater High Speed Pre-coat Trials on Board**

We have demonstrated that, from a rheological point of view, the 14 parts of styrene-butadiene latex can be partially replaced by a natural polymer binder from the Stabilys® range. The number of parts of Stabilys® used allows for the optimisation of the formula and the possibility of replacing all or part of the CMC and synthetic thickening agent without changing the coating colour rheology. Modified natural binders such as Stabilys® influence the viscosity over the complete range of shear rates encountered by a coating colour, as do synthetic viscosity modifiers. CMC is only effective at low rates of shear and does not influence either the viscoelastic behaviour of the colour or its water retention value.

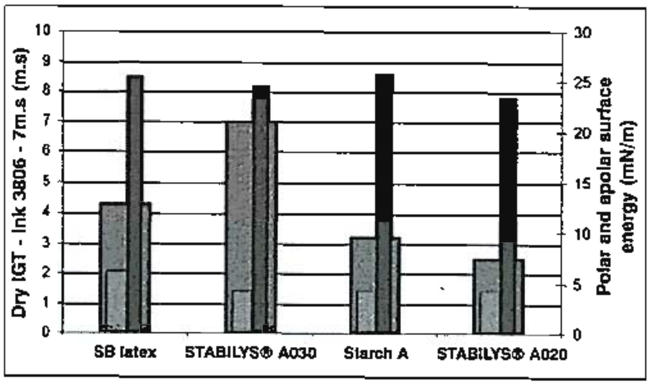

Figure 8: Pick Resistance and Surface Energy

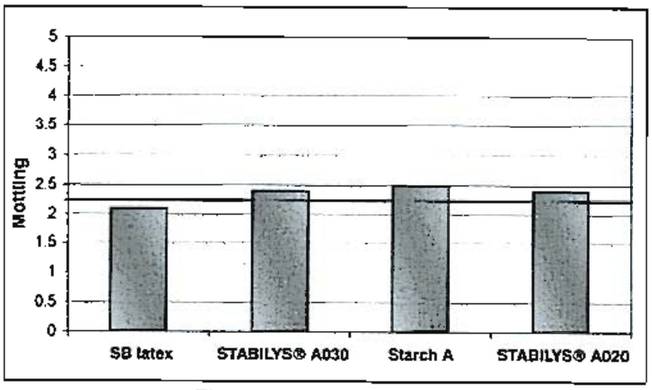

Figure 9: Mottling Index

The characteristics of both the pre-coated and the finished board were examined. Only slight differences were noted between the pre-coated boards in terms of their characteristics: stiffness, Scott bond, smoothness, brightness and wettability. These differences would be later masked by the top-coating when the gloss and stiffness were virtually identical whatever pre-coat formula was used *(Figure 10)*.

A further trial on the Helicoater replacing 6 parts of latex confirmed these excellent results *(Table 6)*.

| | Reference | Trial |
|---|---|---|
| Smoothness (mL/min.) | 149 | 99 |
| Brightness (%) | 82.4 | 83.4 |
| Scott Bond (J/m²) | 205 | 225 |
| Stiffness MD (N) | 524 | 507 |
| Stiffness CD (N) | 270 | 269 |
| Dry IGT (No. 3808 - 2m.s) | 0.82 | 0.82 |
| Wet IGT (No. 3808 - 0.3m.s) | Ink refusal | Ink refusal |
| Formamide penetration index | 0.1 | 0.1 |
| Surface free energy (mJ/m²) | 29.1 | 30 |
| Polarity (%) | 16 | 18 |

Table 6: Finished board characteristics, replacing 6 parts of latex

**High Speed Helicoater Top-coat Trials, Series A**

With Stabilys® A030, the top-coat colour has a higher viscosity throughout the shear range compared to the 100% latex reference formula. The main consequence of this was to require an increase in blade pressure.

The finished paper test results show an increase in the hydrophobicity of the surface, which would normally result in improved offset printing quality. The dry pick strength was he same as the reference, the other characteristics measured showed no significant difference.

**High Speed Helicoater Top-coat Trials, Series B**

Unusually, in this study we did not find an increase in UV brightness as is normally the case with formulas containing starch and other natural polymer binders.

We noted that the board stiffness was improved when the coating colour contains a natural polymer binder. The loss in gloss, except for LAB A & B and Stabilys® A030, was surprising given that the board was not calendered. It is thought that a change in coating parameters was responsible for this.

The surface strength of the board was the same as the reference for LAB's C, D & E. Only LAB's D & E appeared to increase the hydrophobicity of the board's surface.

*Table 7* gives a summary of the parameters analysed after a commercial printing of the boards. The boards are ranked from good to poor (high to low).

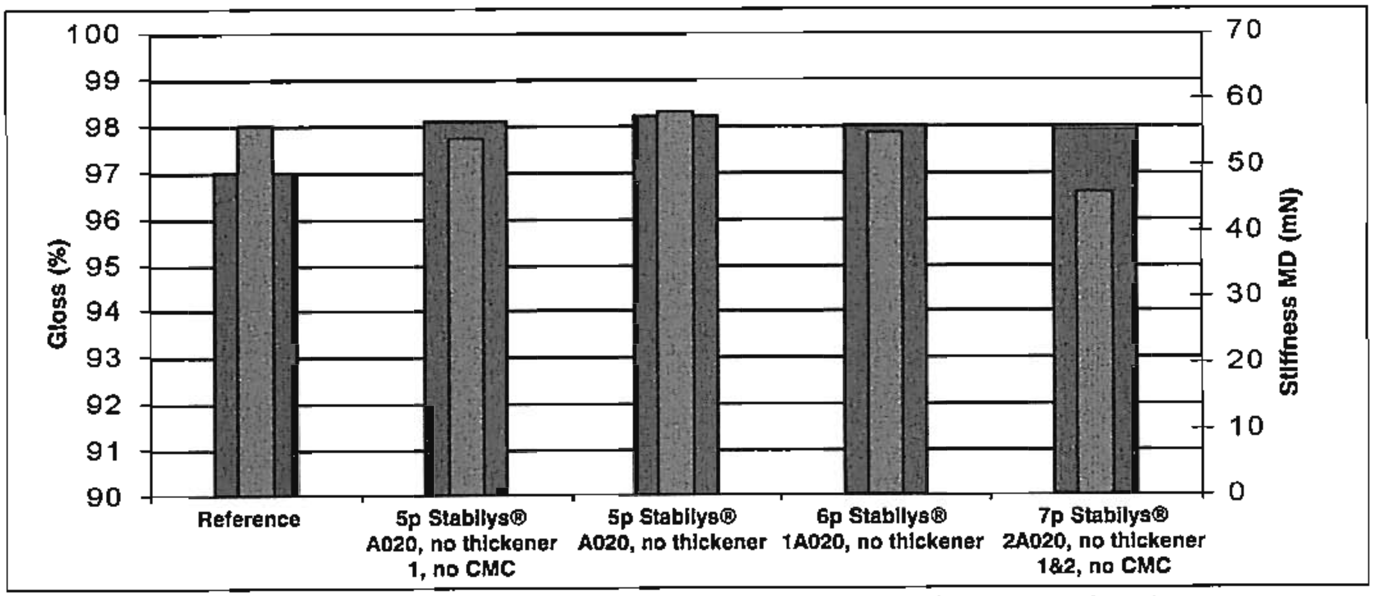

Figure 10: gloss and stiffness of the finished board as a function of the pre-coat formula

| Product | Dot gain | Print Gloss | Ink transfer | Trapping | print through | Mottling | Rub resistance | Set-off | TOTAL |
|---|---|---|---|---|---|---|---|---|---|
| LAB A | 0 | 1 | 2 | 1 | 2 | 1 | 1 | 1 | 9 |
| Ref | 0 | 0 | 0 | 2 | 2 | 1 | 1 | 2 | 8 |
| LAB B | 0 | 0 | 2 | 1 | 1 | 0 | 2 | 1 | 7 |
| LAB G | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 7 |
| S. A020 | 0 | 1 | 1 | 1 | 1 | 1 | 1 | 0 | 6 |
| S. A030 | 1 | 1 | 1 | 1 | 1 | 0 | 1 | 0 | 6 |
| LAB C | 0 | 1 | 1 | 1 | 2 | 0 | 1 | 0 | 6 |
| LAB F | 1 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 5 |
| LAB D | 0 | 1 | 1 | 1 | 0 | 0 | 1 | 0 | 4 |
| LAB E | 0 | 1 | 1 | 1 | 1 | 0 | 0 | 0 | 4 |

Table 7: Offset printing quality of finished boards.

It can be observed that it is feasible to replace a significant portion of the latex by a modified natural polymer binder providing that a suitable product is chosen considering both the rheological properties desired and the base paper. In effect, the products LAB's A, B, G give virtually the same printing properties as the reference and the others were only slightly poorer *(Table 7)*.

**High Speed Pilot Trials**

With Stabilys® A030, the pre-coat colour could be prepared at a higher solids than the reference formula, 68% compared to 67%, whilst still maintaining good handling characteristics at high shear rates. The Brookfield viscosity was slightly higher then the reference. The water retention (Gradek method) was higher with the Stabilys® *(Figure 10)*.

Paper treated with the Stabilys® A030 containing pre-coat was one point higher. This could possibly be explained by the higher coating solids but is this sufficient to change the gloss of the finished paper?

The papers were also checked in the lab for their mottling characteristics, both wet and trapping mottle. Little or no difference was observed in spite of the differences in coating solids *(Figure 11)*.

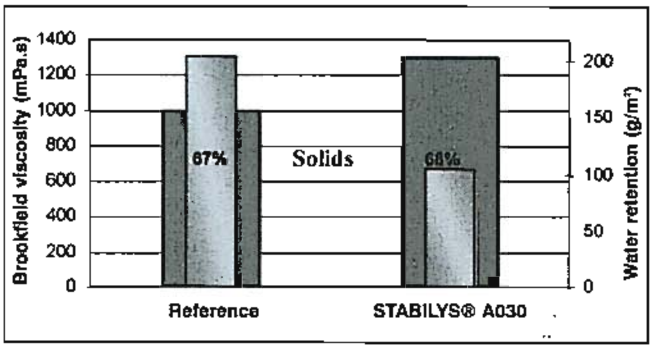

Figure 11: Pre-coat characteristics

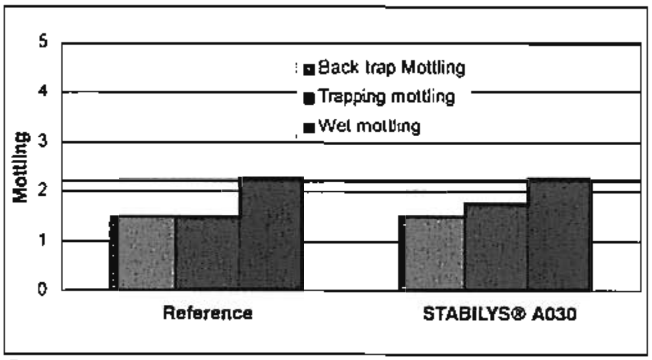

Figure 12: Mottling index of reference paper and paper containing Stabilys® A030 in the pre-coat

## Conclusions

The Stabilys® range of thermally modified natural polymers has proved itself to be suitable for use in pigment coatings for paper and board. It is possible to obtain stable, high solids (up to 42%) binder solutions. Coatings prepared with natural polymer binders have a suitable rheology for current coating technologies, are cost effective and improve the recyclability of the finished papers and boards.

Stabilys® can be used to substitute latex in the pre-coat and top-coat without a loss in dry solids:

- The water retention is better.
- The surface strength is generally equivalent or better; latex tends to remain on the surface of the coating while the natural polymer binder tends to penetrate into the body of the sheet.
- Sheet stiffness is normally improved.
- The gloss of supercalendered papers is lower but the print gloss and print gloss gain is higher.
- There is no significant difference in the degree of mottling.
- The cost savings are significant. The examples presented represent savings of between €2.5 and €8 /tonne of finished paper.

The loss in supercalendered gloss can be compensated for by changing the calendering parameters, by increasing the coating solids (binder solutions concentrations of up to 42% are possible) or by a change in the grade of the natural polymer binder used. A supplementary advantage to increasing the coating solids is a reduction in drying costs (+ 1% in solids ≅ -4% energy cost).

Roquette is actively working on the development of natural polymer binders for non-contact coating methods such as curtain coating and on the problem of misting at the film-press. A new binder was recently tried at KCL on their film-press at 1500 m/min with no evidence of misting, unlike the reference formulation.

## Acknowledgements

We would like to thank CTP for their collaboration in the evaluation of offset printing quality following commercial printing of samples and for their help in developing laboratory methods for offset print evaluation, including print mottling.

We would also like to thank all our colleagues in Roquette Research Centre who have helped with the Dixon coater trials, the rheological characterisation of the binders and coating colours and the testing of the paper properties.

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# NOTES

# Aqueous Dispersions of Polyolefins

*by*
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**Brad Moncla, Wenbin Liang,**
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The Dow Chemical Company

SESSION TWO
PAPER TEN

## Abstract

Polyolefins are used extensively in many industries due to a combination of attractive attributes. To date, these attributes can only be incorporated into finished articles through conventional thermoplastic forming processes such as extrusion, thermoforming, injection molding, and blow molding. Polyolefins have not been available for use via low viscosity application techniques due to the difficulty in polymerizing polyolefins, especially polypropylene, in an aqueous environment.

To address this gap, a novel process has been developed to disperse conventional polyolefins in water. Dispersions of ethylene and propylene based resins have been produced at scale with high solids content and with submicron particle size. When applied to a substrate, these dispersions combine the typical attributes of polyolefins, namely heat sealability, low temperature flexibility, and water and chemical resistance, with the attributes typical of aqueous systems, adhesion to polar substrates and the ability to accept inorganic fillers. Polyolefin dispersions (PODs) can be applied via traditional low viscosity application techniques including printing operations such as rotogravure. This combination of properties makes these materials ideal for use as a laminating adhesive and as a heat sealable coating.

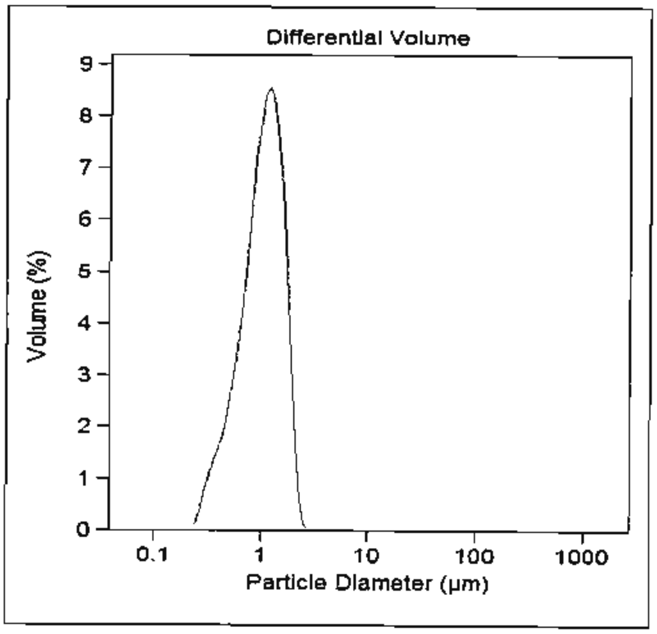


Figure 1. Example of particle size distribution of polyolefin dispersion.

## Mechanical Dispersion of Polymers

A mechanical dispersion technology has been developed to produce water-borne dispersions of polymers that cannot be made by emulsion polymerization. While the focus of this paper will be on mechanical dispersions of polyolefins, it is envisioned that commercially viable mechanical dispersions of other polymer types will be developed in the future. The advantage of the mechanical polyolefin dispersion technology is that there is no solvent used and the dispersion is stable to high solids content.

Under the right processing conditions, the process produces high solids (40-55 wt %) dispersions with an average particle diameter of about 1 micron from olefin homopolymers and copolymers *(see Figure 1)*. The dispersions typically have a viscosity of less than 500 cps at ambient temperature (USP Method 911) and pH ranges from 8.5 to 11.0 (USP Method 791).

## Properties of Polyolefin Dispersions

Mechanical polyolefin dispersions provide the properties of polyolefins in a water-based product that can be processed using many conventional low viscosity application techniques. Some of the attributes that polyolefins exhibit in end-use applications include:

- Water resistance
- Oil and grease resistance
- Heat sealability
- Range of hardness and melting point
- Recyclable
- Thermoformable / embossable
- Elasticity / low temperature flexibility
- Superior adhesion to polyolefin substrates
- Compliant for direct food contact
- Adhesion to polar substrates
- High coefficient of friction (anti-slip)
- "Consumer friendly" chemistry
- Non-allergenic

Many of the desirable attributes of polyolefin dispersions are driven by the semi-crystalline nature of the polymer. *Figure 2* shows the crystalline structure of dried polyolefin dispersion that has not undergone film formation. Crystallinity provides structure for enhanced mechanical strength and flexibility. In addition, the crystalline structure is insensitive to the presence of water and oil and grease, providing good water and oil/grease barrier properties. Many emulsion polymers derive their strength from hydrogen and ionic bonding, which is susceptible to water and oils.

Another attribute of crystalline structure is the presence of melting behavior. Most emulsion polymers are characterized by their glass transition temperature, $T_g$. Polyolefins have a glass transition temperature and a melting point, $T_m$, which is the temperature where regular packing of the crystal lattice disappears. The $T_g$ of polyolefins is typically below -20°C and is the reason for their excellent low temperature flexibility. The $T_m$ of polyolefins ranges from 40 to 160°C and is the more important thermal transition for most converting operations and end-use applications for PODs. The melting behavior of polyolefins is critical to providing the ability to heat seal, thermoform and emboss coatings made from PODs. The level of crystallinity can be tailored to adjust heat sealing temperatures as well as the hardness/modulus of the finished coating.

The low surface energy nature of polyolefins also plays an important role in the performance of polyolefin dispersions. Many polyolefins, especially the homopolymers of ethylene and propylene, are composed solely of carbon and hydrogen *(see figure 3 below)*. The surfaces of articles produced from these polyolefins have low surface energy (often less than 34 dynes/cm) and are very difficult to adhere to. This often presents an issue when building structures based on multiples layers that include polyolefins. The challenge is especially great when using water-based dispersions as adhesives or coatings onto polyolefins. Most monomers used in emulsion polymerization are polar in nature and are not compatible with polyolefin surfaces. Polyolefin dispersions have the advantage of having the same chemical building blocks, or monomer units, as standard polyethylene and polypropylene polymers. This allows PODs to have excellent adhesion to substrates such as unprimed, untreated BOPP (biaxially oriented polypropylene) and HDPE (high density polyethylene). In addition to adhesion, the benign chemical nature of polyolefins allows PODs to be direct food contact compliant and non-allergenic.

The low surface energy coatings possible from PODs are advantageous for adhesion to polyolefins, but this can be problematic for adhesion to paper, foil, and other polar surfaces. To balance the adhesion between polar and non-polar substrates, acid groups are incorporated into PODs. The carboxylate groups provide adhesion to metals and polar polymers such as polyamides. The acid groups also provide enhanced shear stability and compatibility with mineral fillers such as calcium carbonate and aluminum trihydrate.

*Table 1* outlines examples of some of the developmental polyolefin compositions that have been produced. Ethylene and propylene copolymers have been widely investigated in the dispersion process. The melting point of the polyolefin copolymer can be varied by changing the ratio of the comonomers and is a key parameter that influences such properties as film formation and heat seal performance.

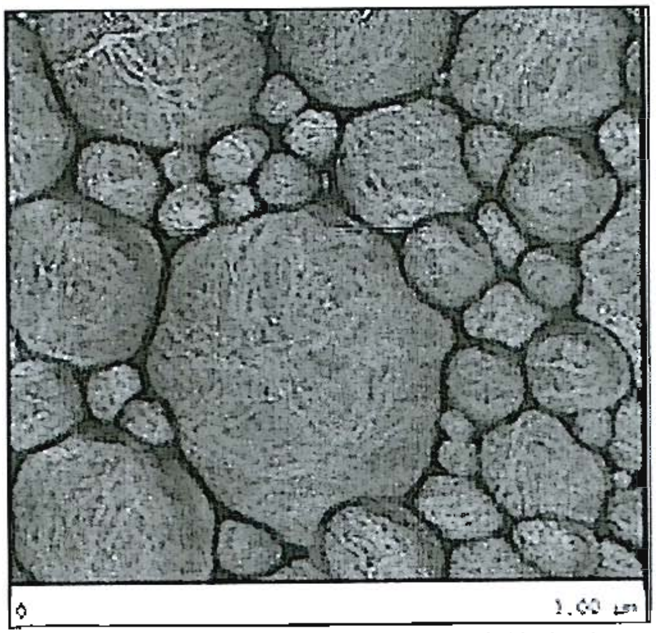


Figure 2. Atomic force micrograph (AFM) of dried polyolefin dispersion showing crystalline structure.

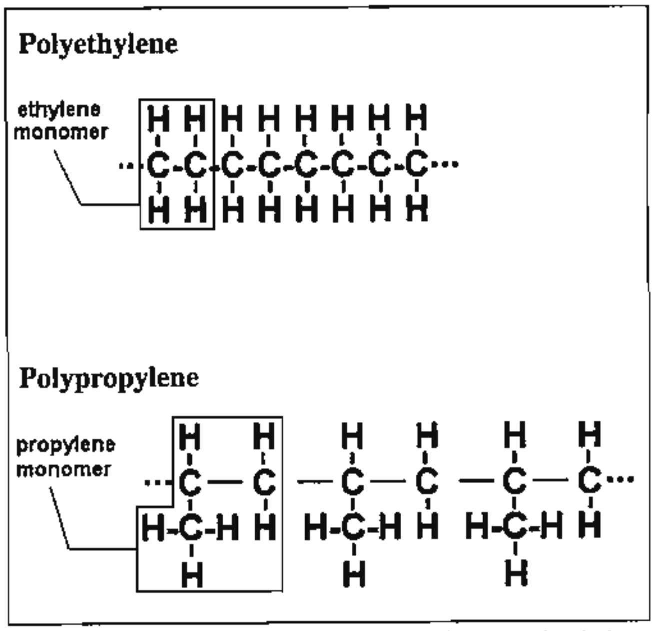


Figure 3. Chemical structure of homopolymer polyethylene and polypropylene.

| Product Designation | Polymer Composition | Carboxylic Acid Content | Polymer $T_m$ (° C) | Polymer $T_g$ (° C) |
|---|---|---|---|---|
| Dispersion A | Ethylene Copolymer | Yes | 60 | -55 |
| Dispersion B | Ethylene Copolymer | Yes | 116 | -55 |
| Dispersion C | Propylene Copolymer | Yes | 85 | -25 |
| Dispersion D | Ethylene Copolymer | No | 60 | -55 |
| Dispersion E | Propylene Copolymer | No | 85 | -25 |

Table 1 – Examples of Developmental Polyolefin Dispersion Compositions

The addition of acid functionality is based on the desired properties of the end-use application. For example, in some applications it is desirable to blend the dispersion with fillers such as calcium carbonate. The ability to incorporate such fillers is particularly important for applications with textiles. In this case, we have found that incorporation of acid functionality in the dispersion formulation is desirable. The ability to incorporate such fillers is particularly important for applications such as carpet backing.

## Film Formation

One key difference inherent to polyolefin dispersions, compared to conventional latexes produced via emulsion polymerization, is film formation. Since the crystalline phase persists until the temperature is increased above the melting point, the polyolefin dispersions are not film forming at room temperature. Conversely, many emulsion polymer latexes have film forming properties at or below room temperature.

Little to no film formation of the polyolefin dispersions occurs until all of the water is driven off, due to evaporative cooling. The coating must then be heated adequately above the crystalline melting point for the particles to melt and coalesce. For many existing converting processes and applications this does not present an obstacle, since in many cases the existing process already encompasses a drying step that operates at elevated temperatures.

Deformation of polyolefin dispersion particles and formation mechanisms of void-free film from discrete particles were investigated in situ using hot-stage tapping-mode atomic force microscopy (TMAFM)[1]. *Figure 3* shows the TMAFM topography images of an ethylene copolymer film cast from Dispersion D, which has a crystalline melting point of about 60 °C. Spherical particles with clear boundaries can be observed. The size of the spherical particles ranges from 0.1 to 3 μm. The unique advantage of TMAFM with hot stage capability is that it allows the monitoring of the particle deformation and inter-particle coalescence processes in real time at the same location.

In order to examine the particle deformation with increasing temperature, a series of TMAFM topography images associated with film formation at elevated temperature are shown in *Figure 4*. Essentially no coalescence occurs at temperatures below 50°C. The particles maintain their shape even up to 60°C. At 70°C, the particles start to deform and a low level of particle coalescence is reached. At 78°C, individual particles essentially disappear with few residual particles still recognizable. The particles become exceedingly diffuse when the temperature is over 80°C.

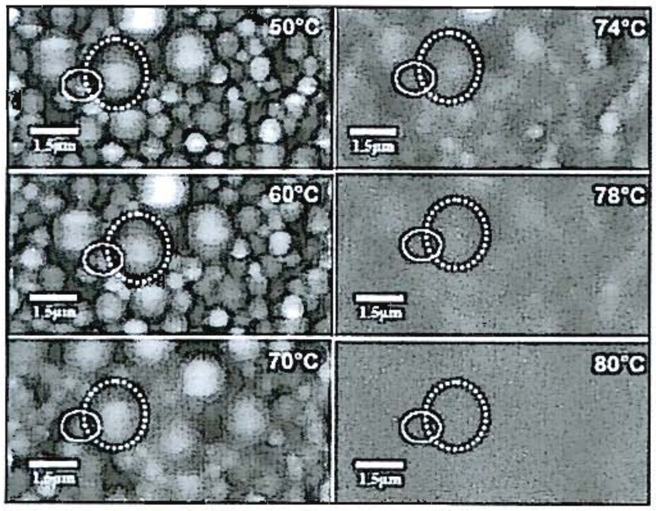


Figure 4. A series of TMAFM topographic images of ethylene copolymer dispersion film at elevated temperature.
(Reprinted with permission from Reference 1)

Under the appropriate drying conditions, the polyolefin dispersions produce films with excellent mechanical properties. *Figure 5* shows the stress-strain curve for a relatively thick (10 mil) film cast from a dispersion of ethylene-octene copolymer, when dried under different conditions. These thick films were dried in a standard forced-air convection oven. Excellent quality films and foams have been produced in continuous processes at conventional processing speeds.

## Conversion Options for Polyolefin Dispersions

Polyolefin dispersions have been processed using many of the traditional converting processes employed with emulsion polymers. As shown in *Figure 6 (overleaf)*, PODs can be (1) air-frothed to produce a foam or foamed backing on various substrates, (2) spray-dried to produce a very fine powder, (3) applied as a very thin coating on a variety of substrates using processes such as roll coating, gravure, spray-coating, and others processes, (4) used to impregnate porous substrates such as woven and non-woven fabrics, etc.

It is also within the capability of this process to disperse compounded blends of polymer(s) with plasticizers, fillers, tackifiers, pigments, stabilizers, and other common thermoplastic compound ingredients. For example high solids, water-based dispersions of hot melt adhesive (HMA) compounds have been successfully produced in this process. These HMAs are typically based on thermoplastic polyolefin elastomer, tackifier resin, wax, and antioxidants. Pigmented polyolefin powder coating formulations have also been dispersed as a precursor to spray drying to produce fine powders.

## Adhesive Lamination and Heat Sealable Coatings

Polyolefins are widely used in the packaging industry as coatings on polymer films and aluminum foil. Typically, polyolefins are applied in the melt phase using processes such as extrusion coating, coextrusion, or extrusion lamination. Often these polyolefin coatings provide a sealant layer or function as a laminating adhesive. The availability of a water-based poly-

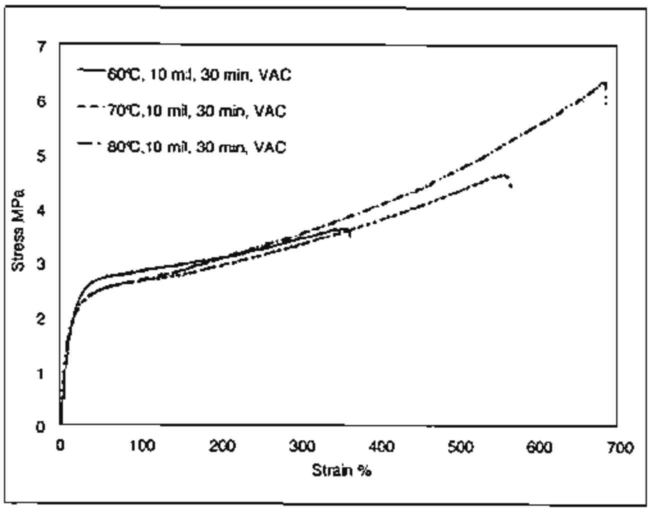


Figure 5. Mechanical Properties of 250 μm films cast from Dispersion D (using different drying conditions in a forced air convection oven)

olefin dispersion allows converters to apply these sealant and adhesive layers using conventional water-based application techniques such as flexographic printing. This can provide advantages such as the ability to apply a much thinner coating than can be achieved with melt processing techniques, the ability to coat at significantly higher line speeds, the ability to coat in a pattern, the ability to apply very low melting point polyolefins with low heat seal initiation temperature, as well as the ability to apply a polyolefin coating at low temperatures. Applying polyolefins at traditionally high melt processing temperatures can sometimes have detrimental effects on the substrate being coated.

## Paper Coating

Oil/grease and water resistance are key properties of paper and carton board that can be improved with the right choice of coating. High levels of oil and grease resistance (OGR) are often needed for demanding packaging applications such as pet food bags, pizza boxes, hamburger wrappers, and the like. Fluoropolymer based coatings provide excellent OGR, but have come under increasing regulatory pressure. This has led converters to search for alternative water-based OGR coatings. Polyolefins are widely used for paper coating, but are typically applied as a thermoplastic melt using extrusion coating techniques. The availability of waterbased based polyolefin dispersions provides an excellent alternative with good OGR performance and economics.

## Paper Oil and Grease Resistance Examples

Water-based polyolefin coatings were made on paper to evaluate the oil and grease resistance of the coating. The dispersion was applied onto the rough side of a Fraser base stock having a basis weight of 59 g/m² using wound rods. A coating weight of 8.9 g (dry) /m² was used. The drying of the dispersion coating onto the paper substrate was performed at 149°C for 5 min. using a convection oven.

OGR was determined by performing a hot oil evaluation. A drop of oil was placed on each sample and the drops were examined at various time intervals to determine the degree to which the oil penetrated to the back side of the sample. Test oils consisted of sesame, vegetable, canola, olive, peanut, corn, and oleic acid. The oils were preheated to 60°C in an oven. A 6 × 7 inch coated sheet was taped onto a PLEXIGLAS® acrylic sheet. A drop of oil was then placed on the sample surface and the time recorded. Samples were then rated on a pass to fail scale, immediately without oil wipe-off. This is the immediate or "I" reading on the test chart.

The pass to fail scale is rated as follows:

P = Pass, i.e. no staining noted on front-side or backside
LS = Lightly Saturated, i.e. stain not through to backside of paper
HS = Highly Saturated, i.e. spreading stain through to backside of paper
S = for complete saturation of the fiber network
A# = Number of pinholes noted in the field of the drop
M = Multiple pinholes in the field of the oil drop

The samples were rated again after one hour at ambient conditions. This reading is indicated as "1" (1 hour) on the test chart. The treated samples were then placed in a 60°C oven overnight. After 20 to 24 hours in the oven, the samples were taken out and the oils wiped off the surface. The back side of the samples were observed through the PLEXIGLAS® acrylic sheet. Staining through to the backside is more easily observed with back lighting. Alternatively, the samples were removed completely from the PLEXIGLAS® acrylic sheet. The total amount of time from initial to final reading was recorded to the nearest 0.5 hour. Hot oil test results are shown in *Table 2*.

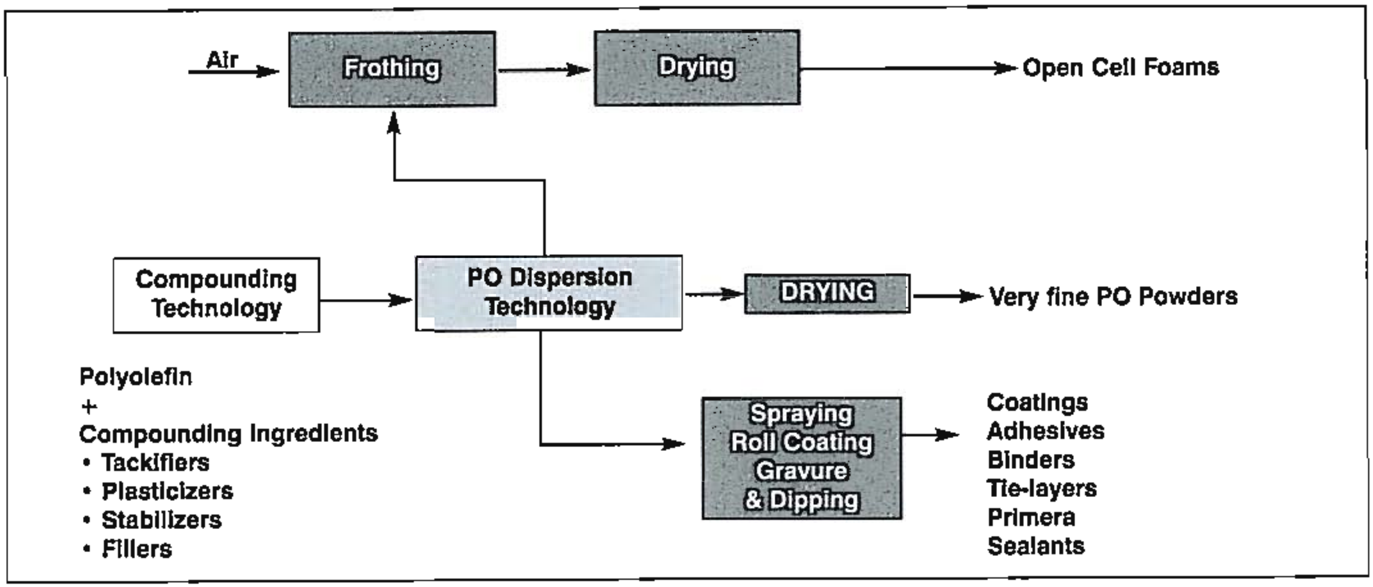


Figure 6. Conversion options for polyolefin dispersions.

| Oil Type | Corn | | | Sesame | | | Vegetable | | | Olive | | | Peanut | | | Canola | | | Oleic | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Exposure (HR) | I | 1 | 24 | I | 1 | 24 | I | 1 | 24 | I | 1 | 24 | I | 1 | 24 | I | 1 | 24 | I | 1 | 24 |
| Polyolefin Dispersion D | P | P | HS | P | A1 | HS | P | P | HS | P | P | HS | P | P | LS | P | P | HS | P | P | HS |
| Polyolefin Dispersion A | P | P | P | P | P | P | P | P | P | P | P | P | P | P | P | P | P | P | P | P | HS |
| Styrene/Butyl Acrylate Latex | P | A1 | HS | P | P | HS | P | P | HS | P | P | HS | P | P | HS | P | P | HS | P | P | HS |

Table 2. Hot Oil Evaluation for Coated Paper Samples

Polyolefin Dispersion A showed superior performance when compared to a commercially available styrenebutyl acrylate latex formulation. It is also interesting to note that the carboxylated POD (Dispersion A), performed significantly better than the acid-free dispersion (Dispersion D).

The polyolefin dispersion can be applied to paper using conventional processes for water based coatings, including various spraying techniques. In addition, the dispersion can be printed onto a paper web, such as by gravure printing, roll coating, etc.

## Paper Moisture Vapour Transmission Rate Examples

The water resistance / absorption of PODs were measured using a Cobb test in accordance with ASTM D3285-93 with an exposure time of 2 minutes. The test involves a known volume of water (100 ml) being poured onto a specific area of the board's surface (100 cm$^2$). Dispersion coatings were applied on kraft paper using a #3 rod and then dried at 120°C. The moisture vapour transmission rates and water resistance of the coated paper samples were then measured and compared to uncoated kraft paper. The board is weighed before and after the exposure and the difference between the two can then be expressed as the weight per unit area of water absorbed in that given time; the lower the Cobb value, the better the result.

The moisture vapour transmission rate (MVTR) was measured using ASTM E96-80 dish test. The test measures the transmission of moisture from a wet chamber through a test specimen (sheet) and into a dry chamber containing a desiccant. The MVTR experiments performed were performed at room temperature with a wet chamber relative humidity of 70%.

*Table 3* shows the MVTR and water resistance via Cobb test for both coated and uncoated samples. In contrast to the OGR, these data show that the acid-free polyolefin dispersions are preferred for water resistance. Blends of acid functionalized and non-acid functionalized formulations can be used to achieve a very desirable balance of both OGR and water resistance in the same polyolefin dispersion coating formulation.

## Frothed Foams and Coatings

Frothed foams can be readily made from polyolefin dispersions, thereby producing structures that are vastly different from foams available from extrusion based foam processes. *Figure 7*, illustrates the lab-scale converting process for producing air-frothed foams from PODs. Continuous foaming on a larger scale has been conducted using readily available equipment employed for froth foaming of conventional latexes. Novel formulation and process technology has been developed

| Dispersion | % Solids | Ambient Brookfield Visc (cP) | pH | Cobb 120 (g/sqm/120 sec) | MVTR (g/sqm/24hr) |
|---|---|---|---|---|---|
| Polyolefin Dispersion E | 50% | 56 | 12 | 1 | 40 |
| Polyolefin Dispersion B | 44% | 510 | 11 | 7 | 420 |
| None | - | - | - | 28 | 950 |

Table 3. Cobb Moisture Resistance of Polyolefin Dispersion Coatings

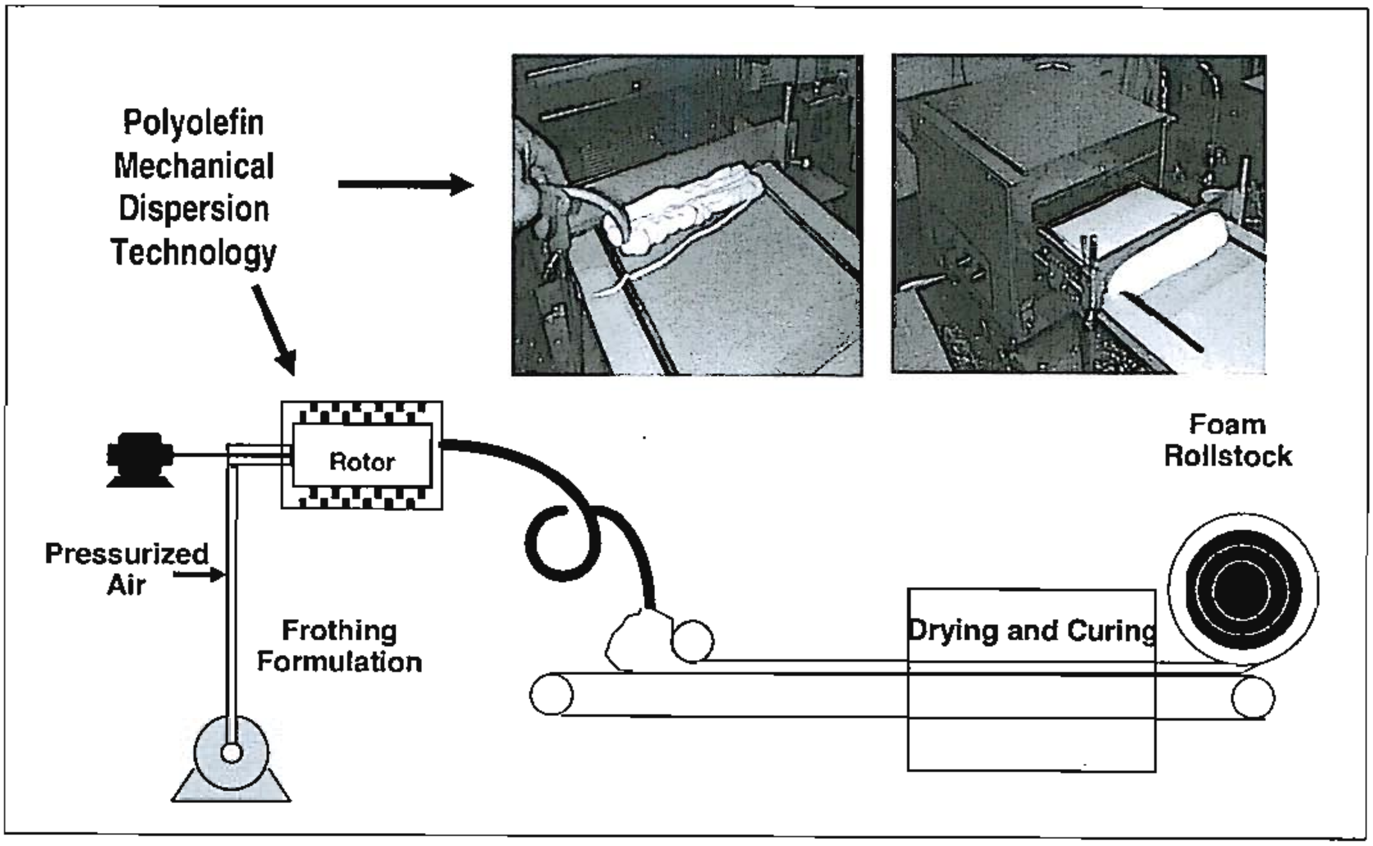


Figure 7. Process for producing frothed foams from polyolefin dispersions.

in order to balance the foaming and drying processes. Achieving this without encountering foam collapse or surface cracking is the key to preparing foams from polyolefin dispersions. These novel foams have the following features:

- Open-cell structure
- High moisture adsorption and "wicking"
- Low compression set at ambient temperature
- High elasticity
- Very soft, luxuriant feel
- Biocompatibility
- Excellent adhesion to polyolefins and other substrates
- High filler loading capability
- Recyclability
- Embossability

Foams can be foamed directly onto a variety of substrates such as textiles and fabrics, non-wovens, carpet, paper, metal, plastic films, etc. A scanning electron microscope picture of frothed polyolefin foam is shown in *Figure 8.*

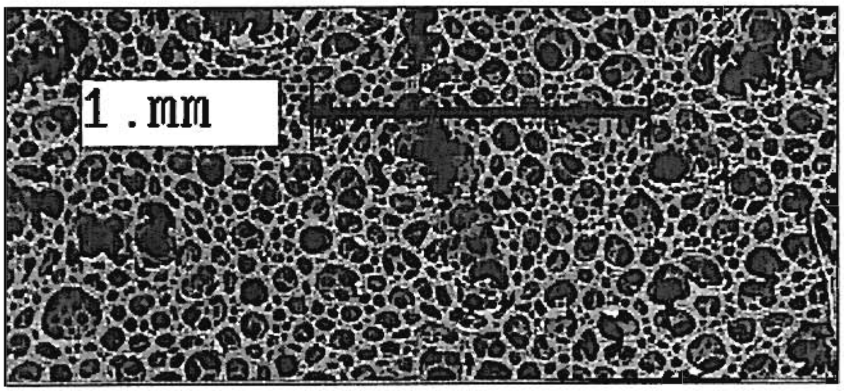


Figure 8. Frothed foam produced from polyolefin dispersion.

## Summary

Thermoplastics, including polyolefins, have many desirable properties in end-use applications. However, extrusion is typically the only viable method for converting these materials into a finished good. A proprietary process has been developed for mechanically dispersing a wide range of polyolefins to produce high solids content polyolefin dispersions with an average particle size of approximately 1 micron. These dispersions can be employed in conventional converting processes typically used for emulsion polymer latexes, including: spraying, froth foaming, roll coating, gravure printing, dipping, impregnation, etc. The polyolefin dispersions offer a unique combination of characteristics not found in typical emulsion polymers. These attributes create significant opportunities for innovation by formulators and converters.

1 Li, Jing, Liang, Wenbin, Chum, Steve, In Situ Monitoring of Dispersion Film Formation Using Tapping Mode Atomic Force Microscopy, MRS 2004 Fall Meeting Proceeding: Vol. 838E O10.19

# Optimization of the Coating Colour Kitchen in the New Environment of the Paper Mills

*by*
**Thierry Leduc**
ABB Cellier

SESSION TWO
PAPER ELEVEN

## Introduction

The paper mill like any company must constantly adjust to the constraints of its market and its environment. In a globalized economy, the industrialist faces fierce competition and often has an out-of-date production tool which is more and more difficult to maintain. The rise in the costs of raw materials and energy necessitates the industrialists to constantly optimise their processes. To ensure production with a stable margin is one of the paper mills major preoccupations.

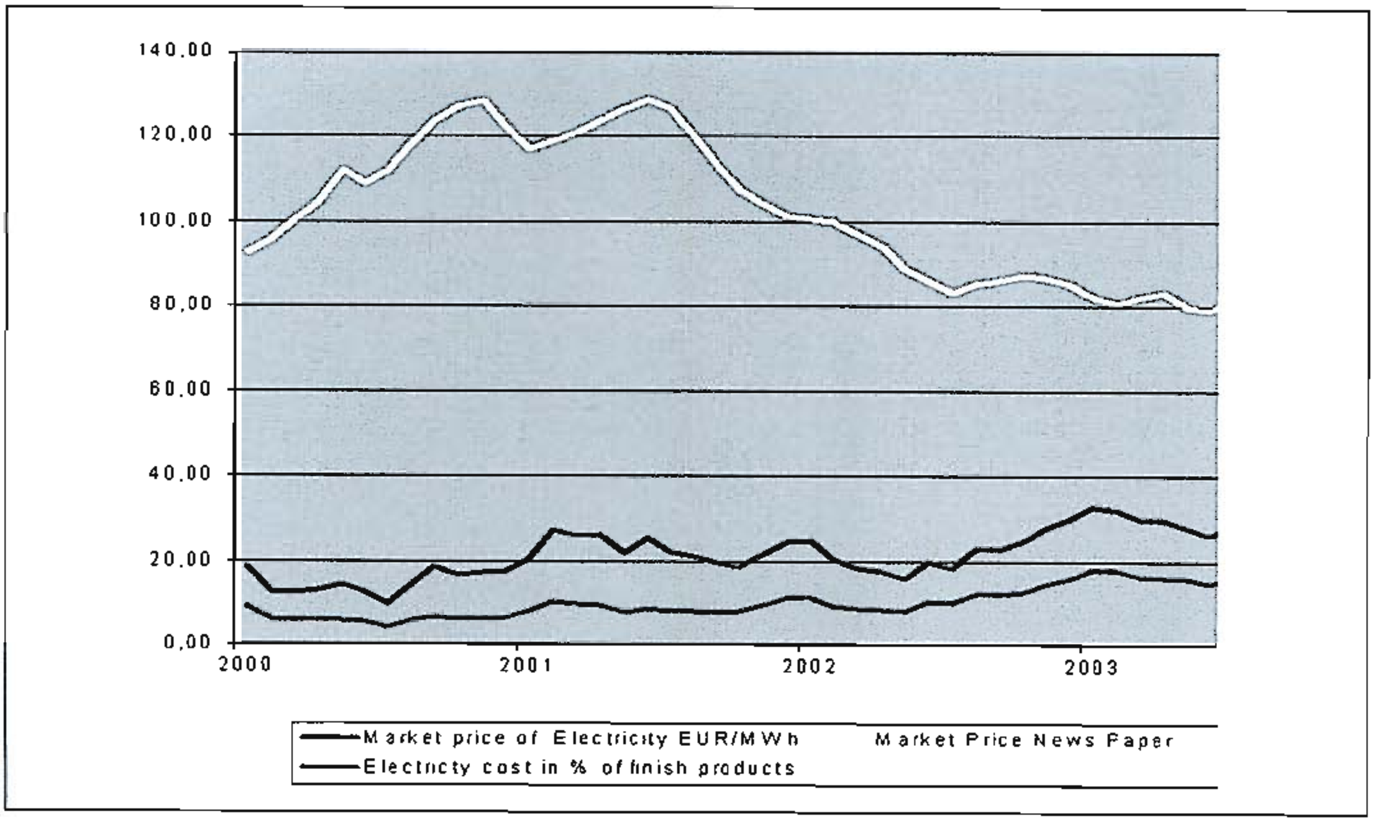
Coating kitchens in paper mills are concerned. Projects for new kitchens in Europe are rare, but modifications, optimizations and revamping are significantly increasing. The engineering business evolves quite rapidly towards a service business where the advice becomes as essential as the supply of equipment.

For the industrialist, the technico-economical justification of an adaptation of the production tool is not always simple. How can we replace what is functioning ? What is the return on investment of the expected change ? All these questions require a detailed assessment of the pertinence of solutions provided on the market.

In this connection, we set out below the most pertinent evolutions/optimizations of coating kitchens regarding this economical logic.

## Energy saving

Energy saving is a topical matter in paper mills. One of the after effects of successive oil crises is that energy is more and more expensive. While the energy cost has doubled in 5 years, the paper price has only or slightly increased. The energy part in the paper cost price has doubled to reach an all-time high of about 20 to 30%.



The capacity of the installations and equipment to control their energy consumption has become a significant criterion of assessment. The coating kitchens and the preparation of chemicals compounds are no exception to this rule.

The coating kitchen comprises many units. The units that consume large quantities of energy are pumps, cookers, mixing and dispersion tanks. Energy is consumed in the form of steam for cookers or electricity with the many motors used on pumps or equipment. For example, a 12 m³ mixing tank for pigment dispersion can have installed powers ranging from 250 to 300 kW.

Reducing energy consumption has therefore become one of the concerns of the supplier of solutions. One possibility consists in modernising the power supply circuits by, for example, using frequency inverters. Inverters consume only the energy necessary and sufficient for performing a process function without waste. They also allow a more flexible use of the coating colour preparation plant.

As far as the process is concerned, a continuous system consumes far less than a batch system. For the batch system, the use of pumps and equipment is discontinuous with a short time of utilisation and large volumes. The dimensioning of the equipment, pumps and motors is more important than for the continuous process. The compactness of the continuous system means it is preferred with respect to the batch technique when the quality obtained and the performance levels can be identical. More generally, the use of more and more concentrated coatings is also a quite efficient way to save energy.

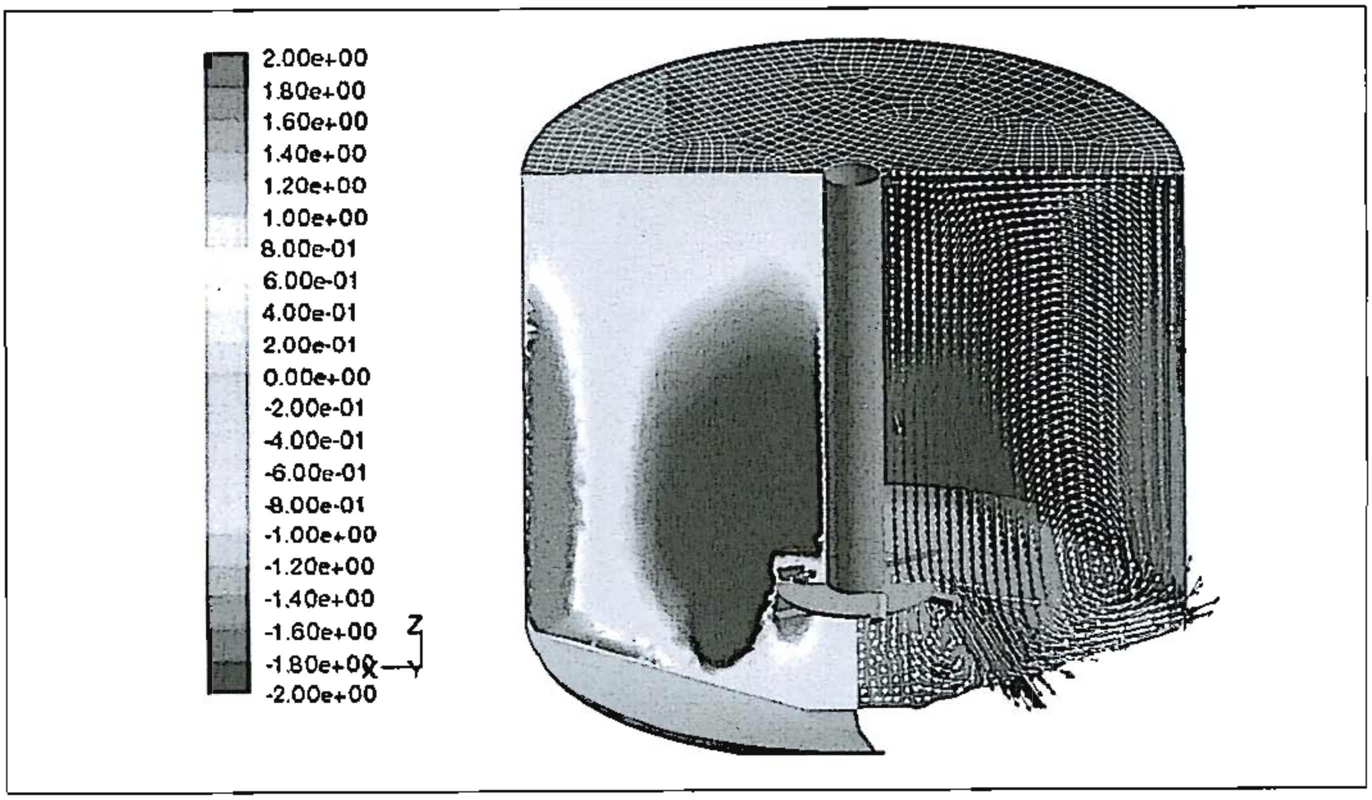
The coating colour manufacturing process itself is optimised to reduce the energy consumption. For example, ABB Division Cellier has developed in conjunction with research centers of the group, a new innovating turbine enabling the energy consumption to be reduced by 20 to 30% when producing coating colour or when dispersing. This type of improvement necessitates thorough simulation studies to determine an optimal operation in a scientific way. Several customers have already modernized their equipment to benefit from energy savings or productivity with a quick return on investment.

## Environmental protection

Environmental protection has become a legal European obligation since 23rd October 2000. The European directive WFD (Water Framework Directive) has a clear objective which consists in reaching the good ecological state of underground and surface waters in Europe for 2015, and reducing or suppressing the rejects of some substances classified as dangerous or very dangerous. In the United Kingdom as in all countries of the EEC, a schedule of measures is fixed every six years (2006, 2009, 2015) with deadlines per district. If these measures announce a tightening of the environmental constraints, a significant effort has already been performed for the treatment of effluents by the paper-makers. A report of SEAP (Scottish Environment Protection Agency) states that a mill in Scotland spends less than £450,000 per year for the treatment of its effluents and almost £1 million for the totality of the water treatment process.

In this field, ultrafiltration is considered as an encouraging solution to reduce the operating costs of the water treatment stations. The principle consists in concentrating the effluents and recycling the solid contents in small quantities in the process.

ABB Cellier has designed and installed several ultrafiltration units in the world. Ultrafiltration units are reputed fragile, however this technique remains very encouraging as this was confirmed by a test programme performed over a year in cooperation with the PALL company in a major French paper mill. The return on investments for this type of installation is 2 years thanks to the savings made with the recycling of dry materials when pre-coating and to the reduction of effluents to be treated. If this technique is currently exploitable for coating effluents, it has not been validated for all effluents and in particular white waters which are the subject of many enquiries.



The effluent treatment is surely not the most satisfactory solution, because it is preferable not to produce them. The quantities to be treated can often be reduced by simply analysing the causes of the rejects. Several leads are to be systematically explored:

- What are the residual quantities at the end of the batch treatment?
- Where are the dead volumes and the low points of the pipes?
- How is the equipment cleaned and with which efficiency ?

This analysis is usually performed in the case of a revamping of an installation because the recent technologies give solutions by choosing the appropriate equipment.

As an example, the cleaning technique with high pressure nozzles has many advantages :

- Reduction of cleaning quantities
- Time saving
- Labour saving.

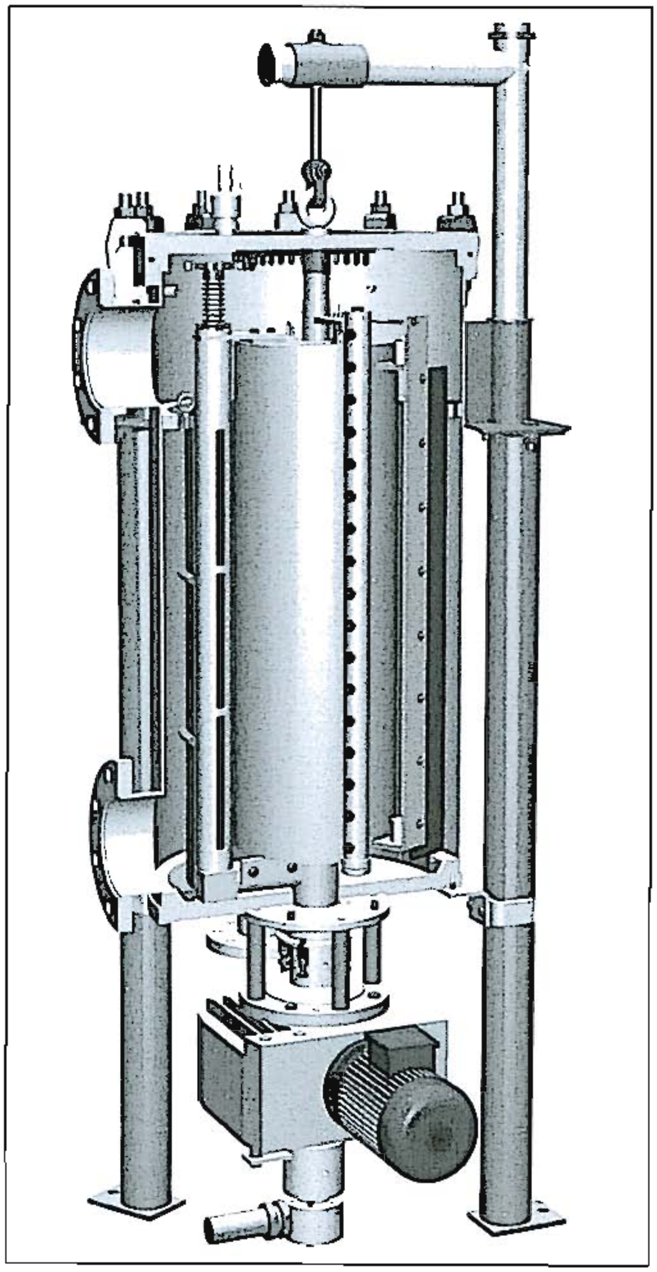


ABB Cellier frequently implements this technique on its Filtercel and its high viscosity mixing units called Delicel.

Similarly, the pigging techniques enable the emptying of the coating transfer circuits and the reduction of lost quantities when rinsing the line. This technique is particularly interesting if the coating kitchen is located far from the coater.

In the same way, a well thought-out planning and a short anticipation on the production ends reduce significantly the effluents between two productions.

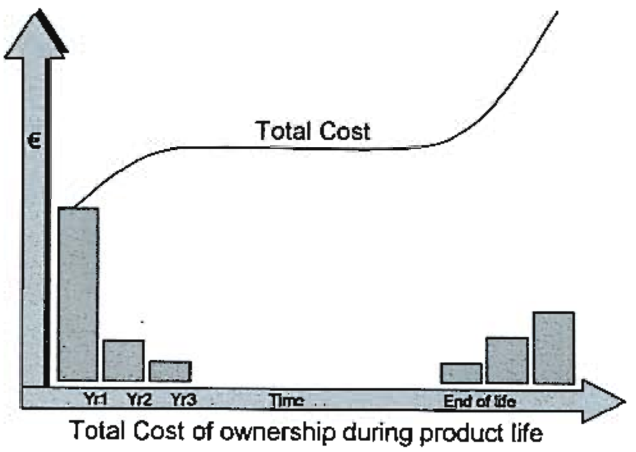
## Reduction of maintenance costs

The efforts of the production sites have also concerned the personnel and the paper mills operating often with a minimum staff. The less strategic tasks have been externalised in order to better concentrate on the trade. One of the sectors the most concerned is certainly the maintenance.

In this connection, all products or solutions enabling the staff to obtain time saving are precious. Products with a long autonomy of use and which do not require much maintenance are favoured. As an example, the pressure filters are now more commonly used than the vibrating filters which are reputed to necessitate much maintenance and frequent cleanings.

Either for the control of the installations or for the maintenance, the modern solutions must assist the operators, simplify and accelerate their decisions. The systems or units must reduce the maintenance necessary to keep them in good working order and provide self-diagnosis functions enabling the operators to intervene only when it is absolutely essential. Automation and supervision meet this requirement, but not many coating kitchens works without production monitoring and in total autonomy.

For its coating kitchens, ABB Cellier division uses a specialised and ergonomic software which benefits from the return of experience of several hundreds of installations. All the paper mills do not have the chance to have such a tool; many paper mills have been equipped more than ten years ago and their production tools are now obsolete in particular the automatisms. The maintenance costs increase because the equipment arrives at the end of its life-cycle, the level of automatism is low and even nonexistent. In that case, modernizing is necessary even if the return on capital invested is not easy to demonstrate. A controlled maintenance is a preventive maintenance which can be planned without unexpected events. The possible stop of the machine due to a failure of an obsolete equipment can sometimes justify the replacement, but the difficulty often lies in assessing this risk ?



Total Cost of ownership during product life

To avoid the problem of obsolescence, a long-term vision is essential. It is advisable to reduce the number of systems, the sets of independent automatisms and to take into account each opportunity of evolution to modernize locally the production tool.

## Adaptability and reaction capability

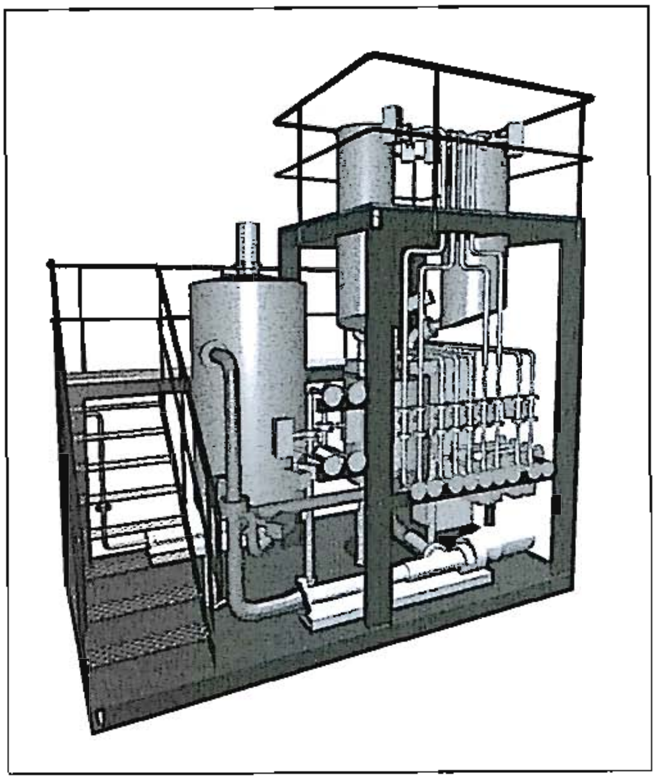
There is no need nowadays to be made aware of the costs of the non-quality. A better control of the quality of a continuous coating process can be understood from two points of view :

- the control of the drifts in continuous operating mode
- the control of the production changes.

For several years, there have been reliable techniques for in-line analysis of quality criteria for coated paper. ABB scanners enable many parameters like shade, gloss, coating weight, etc. to be recorded in real time. These systems offer the possibility to react and to adapt oneself to different in-line measures. For example, it is possible to correct the paper shade by modifying the quantities of dyes introduced at the coating head. But the highly reactive Inline Mini-Batch (IMB) offers the possibility to correlate measurements and formulation.

Combined with in-line systems measuring the paper characteristics (whiteness, gloss, shade,..), a reactive kitchen must offer the possibility to modify rapidly the formulation in order to reach the required quality grade. Production changes are hence quicker, less risky, without losses and cost effective. To guarantee this reactivity, stocks and useless volumes must be reduced to a maximum up to the coating head.

ABB Cellier has designed a new type of coating kitchen called Inline Mini-Batch (IMB) by combining the batch and the continuous techniques. The principle consists in manufacturing a series of small batches to feed a second mixer working continuously. The main advantage of the IMB is to obtain a great flexibility in the formula percentages as well as a significant reactivity regarding the in-line formula change.



The reactivity of this equipment contributes once again to the general objective by reducing the manufacturing costs and by securing the margins.

## Influence of the customer specificity

Each paper mill has its own constraints. A mass production with low added value cannot be compared to a specialised production with a high added value.

In the case of mass production, a shutdown is excessively expensive, the maintenance must be controlled and the obsolescence banished, the saving on effluents is rapid. The coating kitchen must offer a constant quality while saving the components.

In the case of specialised production, batches are smaller, production changes must be rapid and controlled. Production shutdown is more frequent but must remain short. The automatism is generally less sophisticated and the oldness of the equipment less problematic.

With these two examples, we understand that the economical consequences of the choice are specific to each unit. Each project necessitates a thorough analysis and a good knowledge of the site to justify easily the return on investment.

Each necessity of production evolution must be considered as an opportunity to bring improvements in particular to modernize the process, the operation and the automation. The global analysis of the project profitability involves the competence of the supplier of the solution and the project manager who must be able to justify jointly the return on investment.

## Conclusion

All the aspects of the coating kitchen must adapt to contribute to the requirement to make economies in the paper mills. Many possibilities to make savings exist with a short return on investment. The pure engineering business is gradually changing into a service and expertise business enabling the customers to analyse their production tool with an external light. The analysis of the return on investment can be performed only with a close co-operation between the supplier and the production site.

# Cost Reduction through Optimization of Coating Formulations

by
**Mariela Gauto**
Clariant

SESSION THREE
PAPER TWELVE

## Abstract

The coated paper market is diversifying rapidly. However, coating formulations are becoming simpler, in the search for performance and economy.

This paper will demonstrate how to achieve those objectives through a careful selection and addition of coating slurry ingredients, combining novel and traditional technology.

The points to be covered include:

- Wet End vs Coating process control
- Secondary binder selection
- Additives role

## Introduction

The white paper market is quite vast and diverse. Coated grades are also demanding similar requirements seen on the uncoated grades, such as

- higher whiteness
- higher lightfastness
- improved runnability.
- AND lower costs.

Machines are running faster and the chemical technology is also evolving rapidly to catch up with the trend. Optical Brightening Agents (OBAs) cannot be excluded from these phenomenon. They play a key role within the white papermaking process and this role should be thoroughly understood.

OBAs have proven to be very versatile as chemical products. Over the last few years the number of different grades now made with OBA has increased rapidly.

This paper intends to illustrate a way to a more cost-effective and environmentally friendly white papermaking process, selecting and optimising the right ingredients for the final grade.

## Wet End vs Coating: process control

A global internal survey was carried out in 2005 within Uncoated grades ( Printing & Writing, 80-90 gsm ). The aim was to evaluate typical Whiteness of those grades and their composition and to understand market trends.

In terms of Wet End chemistry, it was observed that the higher the Whiteness, the greater the tendency to use disulphonated OBAs. This was not surprising since disulphonated OBAs are more efficient than their tetra counterparts. Disulpho OBAs are more substantive, then extra benefits could be gained, for example:

- process flexibility
- extra product efficiency through less quenchability
- less anionic charge in the backwaters.

Disulpho OBAs can be applied indistinctively in wood-containing or wood-free grades, following certain criteria.

Due to all of the above, disulpho OBAs introduce a great range of opportunities for the papermaker to generate savings within the process. For example, the addition point could be chosen optimising the interaction of the remaining chemicals - see *Figure 1*.

Disulpho OBAs can have a beneficial effect on the backwaters, wherever tetrasulphos are used. Usually, the latter are the first choice due to the lower price/kg. However, when applied in the stock, quite often they reach the saturation point very quickly. This working situation produces an increase of the anionic charge and with it, the whole Wet End chemistry is affected. The change in grades is delayed and runnability worsens. To complicate matters further, the broke level becomes high. When working with coated broke, the picture could become even more complex.

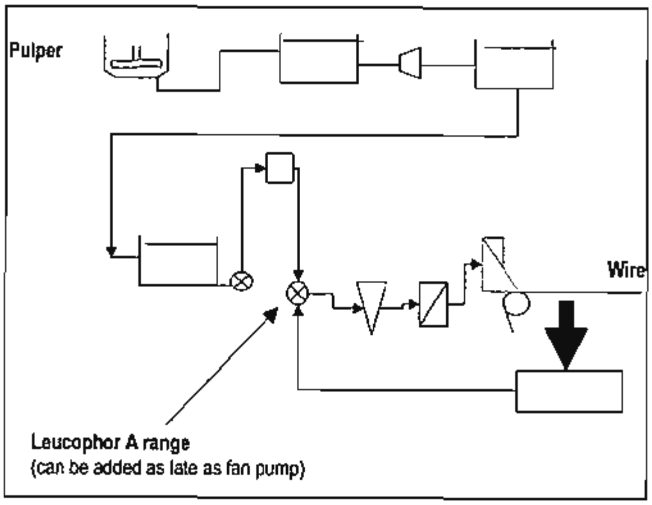


Figure 1 Quick Response

The alternative of using disulphos in the wet end will improve all the above conditions dramatically, bringing extra process control. Particularly improving the total and filler retention - *see Figure 2.*

The market started to see all these benefits. However, at the same time, it demanded a more environmentally friendly product:

| Features | Benefits |
|---|---|
| Urea free | Lower N & COD in the backwaters |
| Solvent, dispersant or glycol free | Lower COD in the backwaters |
| True liquid. | Easy to handle |

Traditionally, it has been impossible to produce a stable liquid with the above characteristics. Clariant has been working on this area for a while. Some attempts were partially successful. Last year a breakthrough was achieved: Leucophor A range ( patent pending ).

Now, it is possible to achieve the same or even better performance than current disulphos, such as Leucophor AHF, with a new range completely friendly with the environment.

The Wet End chemistry needs to be understood throughout. The interaction of the chemicals could cause the sacrifice of some profits.

In wood-free coated grades, savings on total OBA consumption were observed at around 10-20%, through the optimisation of the pre & top coatings OBA additions and applying disulphos in the Wet End.

Other benefits gained:

- greater process control: in some cases, higher Whiteness levels were reached.
- the lightfastness was improved
- solids were increased. This led to a saving in drying energy.

Wood-containing grades are not exempted. The application of OBAs in these types of grades is not new. Indeed use of OBAs in these grades is developing rapidly. Higher Whitenesses are also required, to the extent that many improved newsprint makers are talking about Whiteness instead of Brightness these days. The opacity also can be optimised.

| OBA Consumption | Wet End<br>– 15 to 50% | Size Press<br>– 15 to 40% |
|---|---|---|
| Total Retention | – 5 to 6% | ⬆ |
| Filler Retention | – 10 to 30% | ⬇ |
| Retention Aid | – 5 to 35% | ⬇ |
| Cationic Demand | –>300μeq/l | ⬇ |
| Formation | ⬆ | |
| Internal Sizing | √ | |
| Runnability | Excellent | |
| Grade changes were performed in a few minutes instead of 30-40 mins | | |

Figure 2 Case Study: P&W grade, 80-90 gsm

Lignin is the main problem in these grades. It absorbs UV energy within the same wavelength area as the OBA. The chromophors introduce a yellow shade. All this affects the OBAs performance – *see Figure 3.*

However, disulphos OBAs develop higher brightness against their tetrasulpho counterparts under the same conditions. Savings could be considerable, depending on each particular situation.

It is clear that disulphos have introduced more flexibility and potentiality to these types of grades, providing they are handled in a focused Wet End versus Surface optimisation.

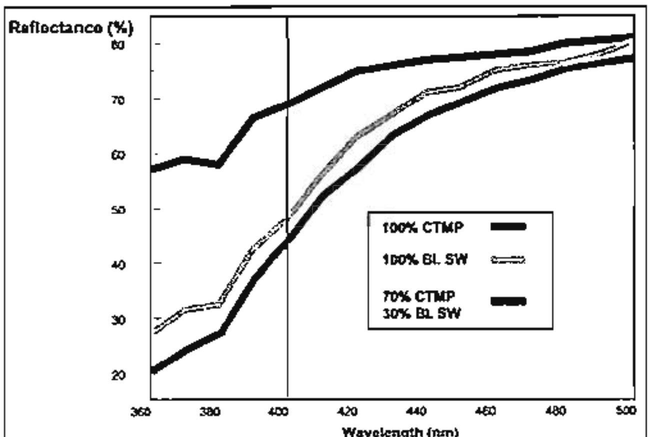
The next sections will cover other additives.

## Secondary binder selection

This is a very interesting and critical area. As it is well known, OBAs need hydroxy groups to work. Secondary binders are the support for the OBA in coating applications. They have different chemistries. In consequence, OBAs will react differently with each of them.

The type of secondary binder and amount should be carefully selected to maximise the OBA performance - *see Figure 4.*

While the development of different properties are sought (i.e, gloss, printability, water retention), lightfastness still is a must have. With the careful selection of the secondary binder, this property could be improved. - *See Figure 5 & Ref 1.*



CTMP = CTMP @ 25 SR
Bl. SW = Bleached Sulphite Softwood @ 25 SR

Figure 3 Fact 1: UV Absorption of wood containing papers

■ OH groups are arranged in different positions
■ Different methods of attachment = different interactions

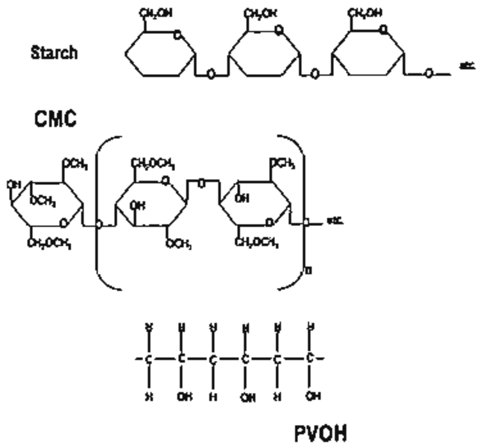


Figure 4 Secondary Binder – OBA Interaction

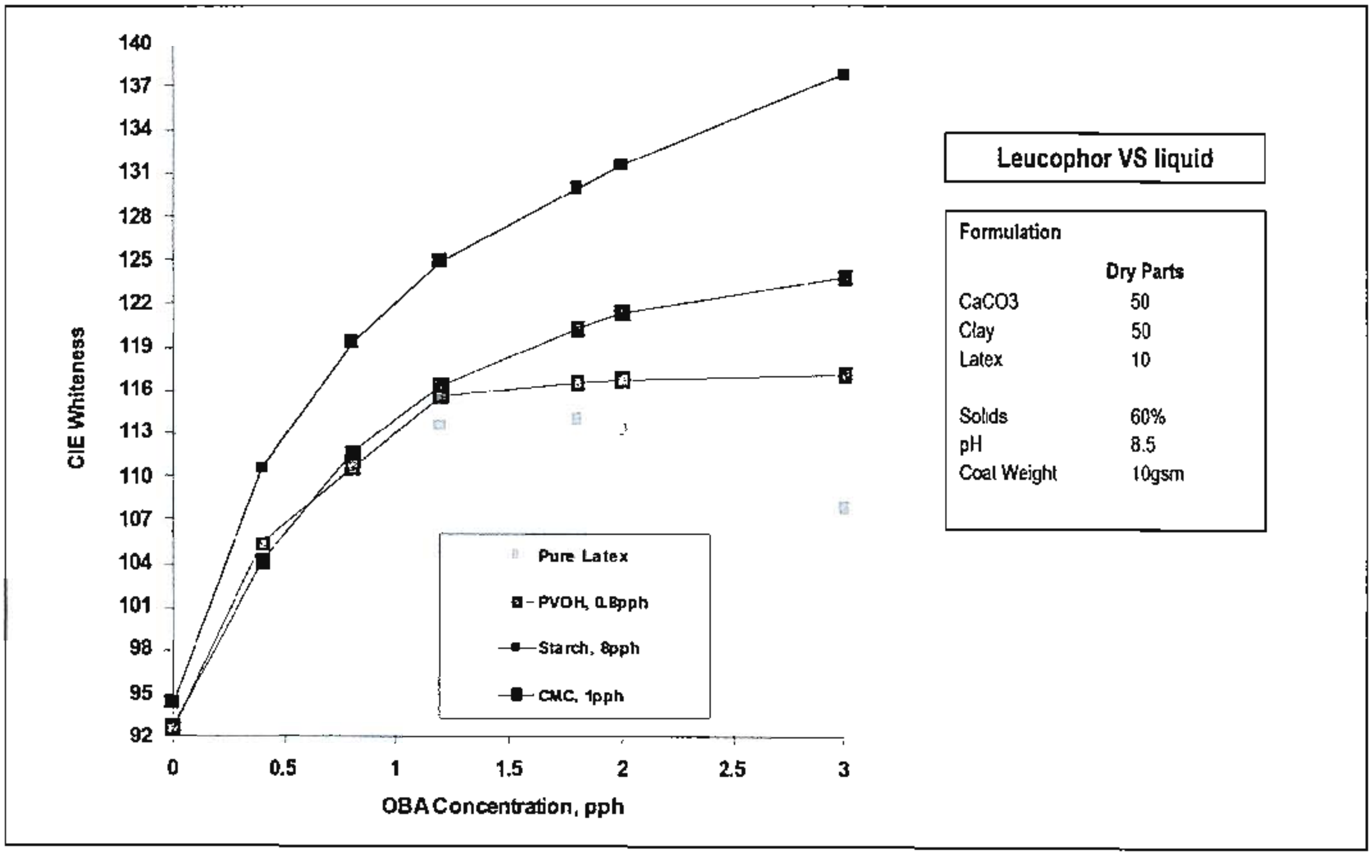
## Additives role

We are analysing the most expensive ingredients of the coating formulation. However, the ones that could maximise the efficiency of coated papermaking the most.

Studies have been carried out with several thickeners and shading colorants.

It has been observed that correct selection of a thickener could lead to an improvement of the water retention and that this thickener combined with the right OBA for the formulation in question, could boost the whiteness to higher levels. This analysis will certainly generate savings - *see Figure 6.*

Clariant understood this and had worked in developing also a more flexible and efficient OBA range: Leucohpor V range.

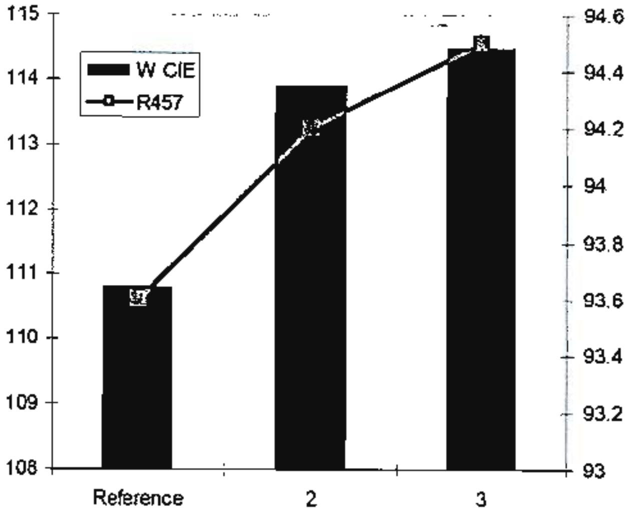


Formulation

| | Dry Parts |
|---|---|
| CaCO3 | 50 |
| Clay | 50 |
| Latex | 10 |
| | |
| Solids | 60% |
| pH | 8.5 |
| Coat Weight | 10gsm |

Figure 5 Effect of Secondary Binders on OBAs (cont.)

| Formulation | Reference | 2 | 3 |
|---|---|---|---|
| $CaCO_3$ | 100 | 100 | 100 |
| Latex | 13 | 13 | 13 |
| Thickener 1 | 0.06 | 0.06 | |
| Clariant Thickener | | | 0.02 |
| PVOH | 0.2 | 0.2 | 0.2 |
| Leucophor UO | 0.8 | | |
| Leucophor VF | | 0.6 | 0.6 |
| Others | 0.76 | 0.76 | 0.76 |
| | | | |
| Solids (target) % | 68.5 | 68.5 | 68.5 |
| pH (target) | 8.3 | 8.3 | 8.3 |



**OBA optimization (type and amount) should lead to a more effective System**

**Total savings: 25% OBA + 65% Thickener**

Figure 6 Thickeners and OBAs

The range cover all the needs:

- Reduction in dosages could lead to considerably savings in drying energy *(see Figure 7)*
- FDA and BfR applications have an alternative
- And others.

However, the plus came through a different angle: Lightfastness. They certainly improve this property - *see Figure 8.*

The studies also covered shading colorant. Often is forgotten the effect of the OBA on the shade. The coordinated optimisation could lead to a whiter paper, with a good lightfastness and good visual appearance.

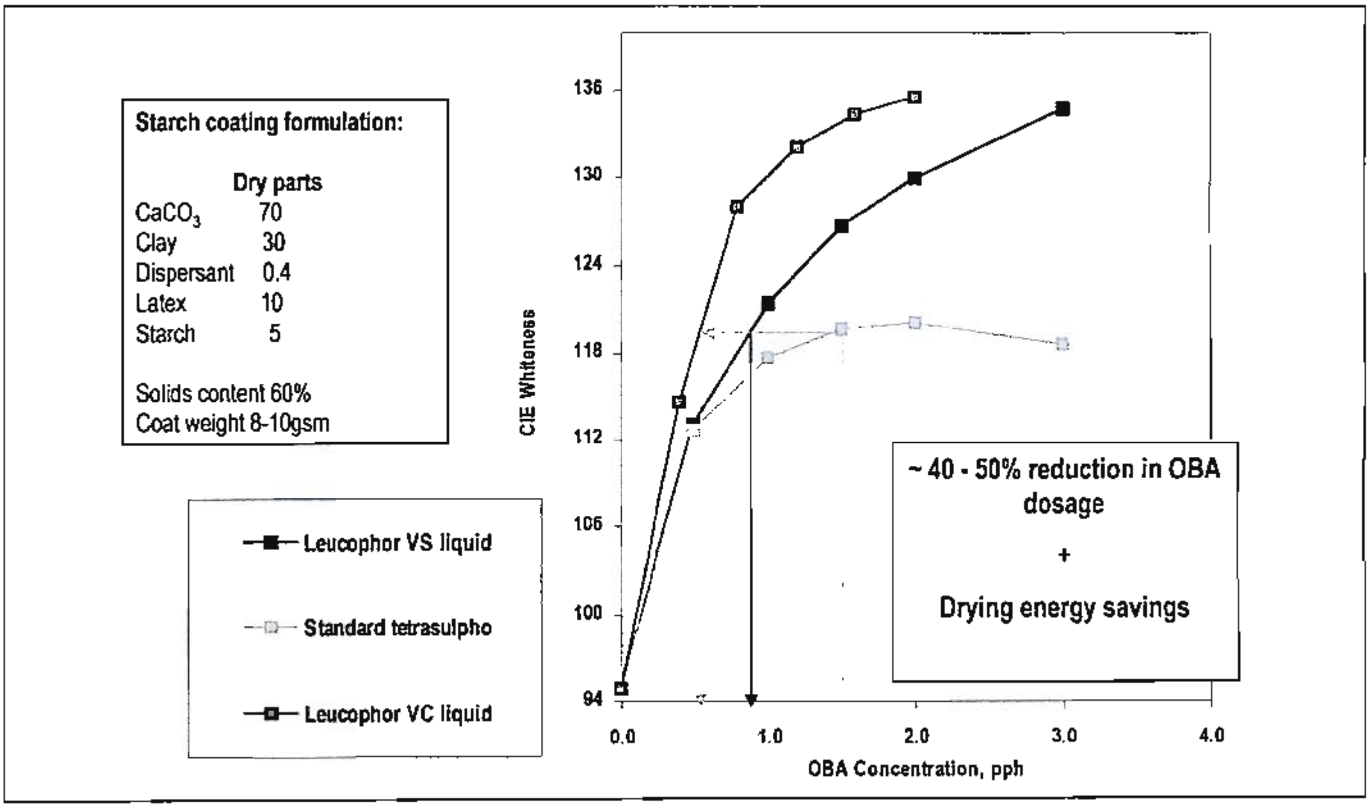


Figure 7 Starch Application – Leucophor VS,VM & VC liquid

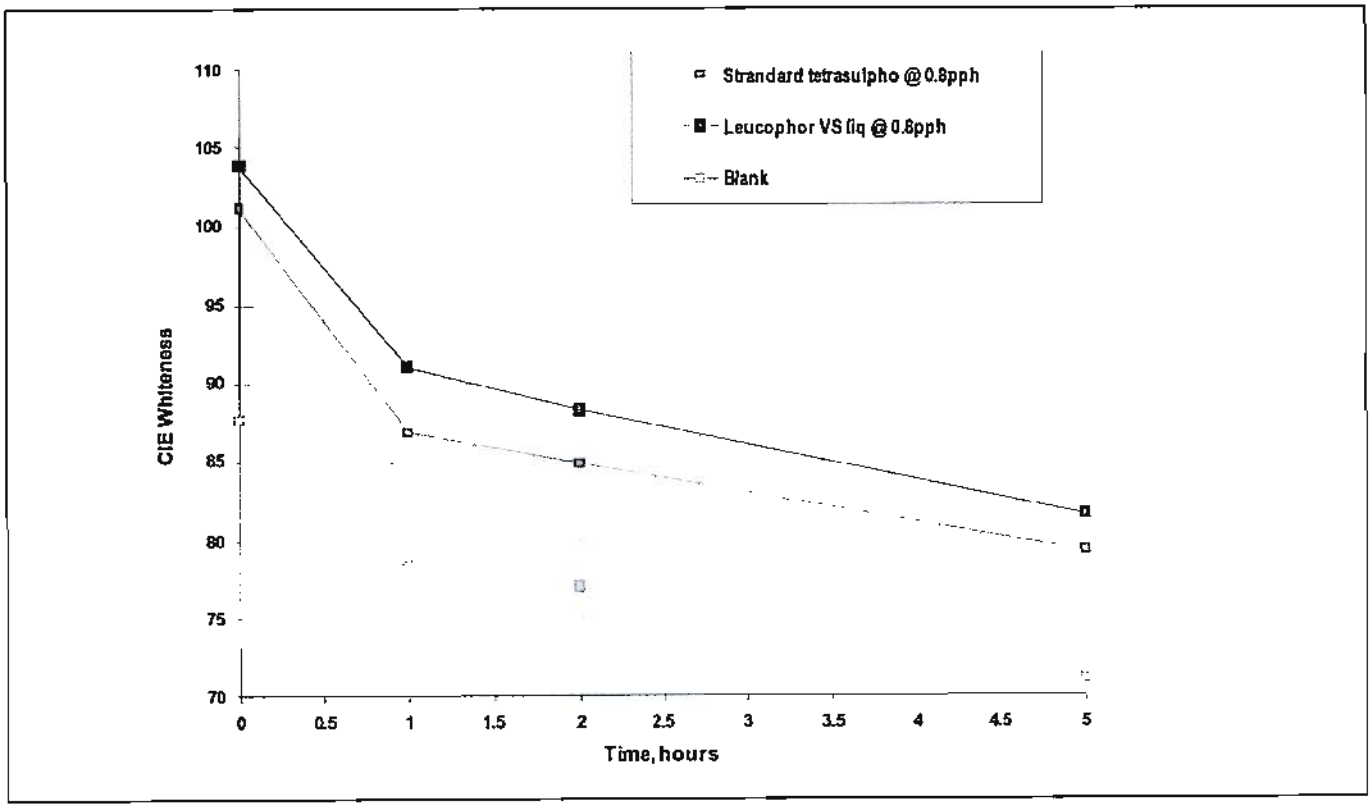


Figure 8 Pure Latex Coating – Lightfastness (Xenon Test)

## Conclusion

The studies concluded that there is an interaction between some of the coating ingredients that affect whiteness, in some cases this is physical in others optical.

A good understanding of the impact on the final paper whiteness grade of each of these interactions, both individually and collectively, will lead to substantial savings and process control improvements.

## Acknowledgments

Thanks to Clariant's Global Head of Product Management Paper OBAs, Alec Tindal and both the R&D and Applications groups at Horsforth for helping in developing new technology that introduces a whole new approach to White Papermaking.

Thanks also to our colleagues spread all over the globe, who believed in this technology and are making it possible for a dream to come true!

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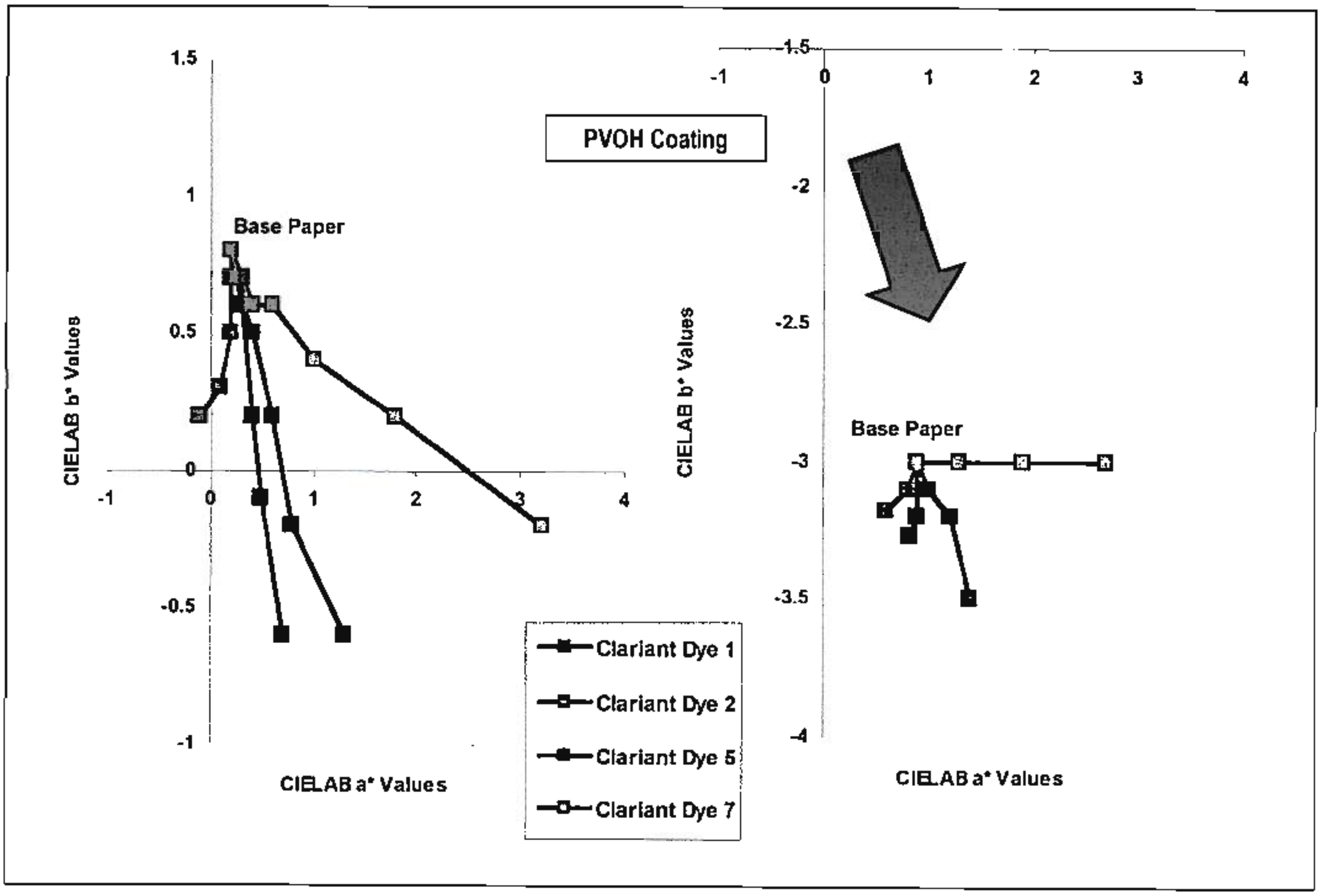

Figure 9 OBAs and Shading Colourant

# NOTES

# Effect of Water Retention and Rheology Modifier (WRRM) Chemistry on Paper Coating Structure

SESSION THREE
PAPER THIRTEEN

*by*
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## Abstract

Synthetic water retention and rheology modifiers (WRRM's) are gaining increasing acceptance in the paper coating industry. Their intended function is to provide an optimum rheological behavior in a range of shear rates and water retention of the coating colour. Optimal thickener dose and chemistry will thus provide certain flow characteristics and water retention properties required for coater runnability and coating structure. In the latter case, it is crucial to understand the influence of the WRRM's on the interactions in the dispersion that cause relevant physical and chemical properties of the coated sheet.

Recently it was demonstrated that the synergistic effects induced by WRRM chemistry could influence the coating structure of the coating colour, particularly the distribution of the coating ingredients along the Z-direction. Optimal interaction prior to immobilization is a critical phenomenon necessary to avoid the strong particle co-aggregation or depletion, which can occur on both the lateral (X-Y) plane as well as along the depth (Z-direction). These findings enable opportunities to further tailor coating structures, via the control of shear-dependent interactions between the various coating ingredients.

In our continuing efforts to improve the fundamental understanding of mechanisms important in dewatering of coating colours and the subsequent formation of the coating structure, particularly the surface morphology of coated sheets, the coating formulations evaluated earlier were applied on a pilot coater (CTC, Raisio, Finland), on a woodfree base stock. These coated sheets were subsequently printed using sheetfed offset inks on a commercial printer (FPC, Raisio, Finland).

Latex distribution both on the X-Y plane and in Z-direction showed local concentration variations, which can be partially ascribed to the particle-thickener interaction state prior to the consolidation and immobilization of the coating layer. Latex concentration on the surface, determined semi-quantitatively from SEM images, indicated small differences between the samples, which seemed to affect the physical-chemical properties of the coated sheets. A method to estimate the ink film thickness based on image analysis is presented. Based on the results, we demonstrate that the ink film thickness can be controlled indirectly via appropriate choice of WRRM chemistry.

## Introduction

Conventional cellulose based thickeners and alkali-swellable polymers (solution or emulsion) are used in coating formulations to provide water retention and certain flow behavior. Anionic charged polymers with conventional chemistry, for example, are known to increase the liquid phase viscosity, without inducing associative particle-particle interactions in the coating formulations[1]. Associative thickeners or nonionic thickeners, on the other hand, may be designed to promote interaction between the various particles of the coating colour, thereby creating a "wet interacting structure" with particles immobilized in a 3-D network at low shear rates, leading to enhanced Brookfield Viscosity. At higher shear rates, however, the structure breaks down providing shear-thinning behavior of the coating colour.

The increased use of narrow particle size distribution (NPSD) ground Calcium Carbonate (GCC) slurries in the paper industry has established a need for more efficient water retention and rheology modifiers[2][3]. In a recent work, we demonstrated that tailored physical-chemical properties of the thickener will not only provide thickening but also ability to control the distribution of pigment and binder particles within the coating structure[4]. Optimal interaction prior to and during immobilization is thus a critical phenomenon in order to avoid strong particle co-aggregation or depletion, which can occur on both the lateral (X-Y) plane as well as along the depth (Z-direction) causing uneven distribution of coating ingredients. Such uneven distribution has been cited as a cause for mottling[12]. The recent findings enable new opportunities to tailor coating structures through controlled interactions between the various coating ingredients, primarily between pigments, latex and also pigment-latex. Nevertheless, the added value to such ability to fine-tune dry structure formation can be gained when understanding its impact on coating structure, surface morphology and end-use, viz., effect on print quality. While the effect of coating structure and porosity on ink and ink constituent absorptivity has been addressed in several studies[5][6][7], it might be worthwhile to include the ability to reduce ink absorption through optimized binder design[8]. The latter is not solely proper design but also optimized concentration and in particular at the surface of the coating.

The scope of this study was to gain a fundamental understanding of mechanisms dominating in the formation of coating structure and distribution of coating components and its impact on surface morphology and ink absorptivity. The coating formulations prepared in the work has been evaluated earlier[4][5]. A pilot blade coater (CTC, Raisio, Finland) was used to apply the coatings on a woodfree base stock. The coated sheets were subsequently printed using sheetfed offset inks on a commercial printer (FPC, Raisio, Finland).

## Experimental Plan

The coating formulations are presented in *Tables 1 and 2*, and have also been discussed in previous studies[4][5]. These were coated on a woodfree base paper using a roll applicator and blade coater. The coating formulations were targeted to a Brookfield Viscosity (100 RPM) of 1250 ± 100 mPas. Some key physical properties of the wire side of the base paper are described in *Table 3*.

The coating parameters from the Pilot Coater are summarized in *Table 4*. The coated sheets were calendared offline under conditions summarized in *Table 5*. The coated sheets were subsequently printed on a sheetfed offset machine, seen in *Table 6* with target print densities.

The coating colours from the pilot coater trial were also wet pressed and the tablets analyzed by ToF-SIMS to determine the local distribution of especially latex. A secondary objective of this analysis was to demonstrate continuity between this study and the previous study[5].

The coated sheets were analyzed using a Scanning Electron Microscope to semi-quantitatively evaluate the area-% latex and pores on the coated sheet surface. SEM images were analyzed using 5 kV accelerating voltage and 15 mm working distance in magnification 5000x. Osmium Tetra Oxide ($OsO_4$) staining was used to label SB latex on the surface and in the cross-section samples and to separate three phases from the backscatter image. Pigment, latex and pore phase were separated due to their gray values and area percentages were calculated with analySIS 5.0 software[10].

| **Description** | **Woodfree base stock for pilot coater trials** |
|---|---|
| **Basis weight** | **73 g/m²** |
| **Caliper** | **100 μm** |
| **PPS (10 kg) [μm]** | **5.01** |
| **Gurley Porosity [μm/Pa.s]** | **10** |
| **Brightness (ISO) [%]** | **89.5** |

Table 3. Description of the base paper (roughness, porosity and brightness measured on the top side)

**Coating Process**

- **Pilot Coating at the Coating Technology Center (CTC), Raisio, Finland**
- **Coated 2 sides (C2S)**
- **Roll Applicator, blade metering**
- **Blade Angle: 42°**
- **Speed: 1200 m/min**
- **Smoother side coated first**
- **Moisture target:**
  - **Pre-coat or dingle coat: 3.5-4.0 wt%**
  - **Top-coat: 4.0-4.5 wt%**
- **Coatweights:**
  - **Single Coatings: 11 + 11 and 13 + 13 g/m²**
- **Drying:**
  - **Pre-heater + 2 IR driers + 3 Air-Foil driers**
  - **Pre-heater: 260 cm before blade**
  - **IR Driers: 230 cm (1st) + 440 cm (2nd) from blade**
  - **Air Foil: 620 cm from blade**

Table 4. Summary of the parameters from coating operation

| | | **Single Coat** | | | |
|---|---|---|---|---|---|
| **Name** | **Description** | **1** | **2 (i)** | **2 (ii)** | **3** |
| **CoverCarb 75** | **GCC (72% slurry)** | **100** | **100** | | **100** |
| **Latexia 302** | **SB Latex (50% emulsion)** | **11** | **11** | **11** | **11** |
| **FF602** | **WRRM (see Table 2)** | **1** | **-** | **-** | **-** |
| **CTA161** | **WRRM (see Table 2)** | **-** | **1.2** | **0.7** | **-** |
| **CTE401** | **WRRM (see Table 2)** | **-** | **-** | **-** | **0.35** |
| | **Solids (wt%)** | **63.9** | **64.2** | **64.0** | **64.2** |
| | **pH** | **9.0** | **9.0** | **9.1** | **9.0** |
| | **Brookfield Viscosity @ 100 RPM [mPa.s]** | **1260** | **1180** | **772** | **1328** |
| | **Capillary Viscosity @ ā = $4 \times 10^5$ $s^{-1}$[mPa.s]** | **68** | **90** | **-** | **42** |
| | **Static Water Retention (ÅA-GWR) [g/m²]** | **133** | **134** | **155** | **156** |
| **(Note: Coating #'s 2 (i) and (ii) could not be run on the coater but are included here for reference)** | | | | | |

Table 1. Coating formulations and characterization

| **Cobinder Name (code)** | **Supplier** | **Chemistry** | **Wt.% solids** | **Ionicity** |
|---|---|---|---|---|
| **FinnFix® 602 (FF602)** | **CP Kelco Oy** | **CarboxyMethyl Cellulose** | **dry powder** | **Anionic** |
| **Rheovis® CTA-161 (CTA-161)** | **Ciba Specialty Chemicals** | **Acrylic Solution Polymer (AS)** | **16.5%** | **Anionic** |
| **Rheovis® CTE-401 (CTE-401)** | **Ciba Specialty Chemicals** | **Emulsion Polymer (HASE-type)** | **40%** | **Anionic** |

Table 2. Detailed description of the WRRM's (Water Retention and Rheology Modifiers) used in the study

Further, the printed sheets were analyzed for the thickness of the ink film. The images were analyzed using magnification 1000x of cross-sections of printed papers. Cyan colour area was separated from the colour image using threshold, colour separation and filter operations. Ink thickness was calculated with analySIS 5.0 software by overlaying grid to separated cyan layer and calculating length of the lines[10].

**Calendar Conditions**

- OPTILOAD at the Coating Technology Center (CTC), Raisio, Finland
- Offline at 8000 m/min
- 2 nip soft calendaring
- Surface temperature: 120oC
- Line load: 80-40-60 kN/m

Table 5. Summary of calendering conditions

**Printing Process**

- Pilot printing at the Future Printing Center (FPC), Raisio, Finland
- Heidelberg CD-74 (sheetfed offset)
- 4-color printing @ 8000 sheets / hour
- Inks:
  - Fast setting: Flint-Schmidt Arrowstar
  - Slow setting: SICPA Tempo Natur
- Target color density:
  - Black: 1.75
  - Cyan: 1.45
  - Magenta: 1.40
  - Yellow: 1.35

Table 6. Summary of the printing process

## Results and Discussion

### Wet and dry coating structure: laboratory and pilot coater study

In the previous study[5], it was reported that the WRRM's display different water retention behavior in the formulations comprising 100% engineered calcium carbonate pigments. Coating formulations targeted to the same Brookfield viscosity, displayed different water retention and different shear dependent rheological properties[4]. Partly, these observations were expected due to specific functionality of the WRRM's. One area of focus in this study was to confirm observation made in laboratory scale[5], with findings observed from the Pilot coater trial.

*Figure 1A* presents the effect of WRRM's on the blade pressure difference recorded at the start and the end of the short pilot run, respectively. In case of the CTA161, the blade pressure increased to the limit, as presented in *Figure 1B*, and therefore the blade pressure difference is not representative. However, the values presented here are mean values from top and back side coating. From the data, it appears that at the lower coat weights, the difference in blade pressure becomes more dependent on the interaction induced by the WRRM's used in this particular formulation. Obviously the pressure under the blade becomes slightly higher at lower coat weights, which causes a shear stress induced breakdown of the interacting structure leading to depletion of certain constituents. This is accompanied by the characteristic properties of the base paper thus reflects the performance of the WRRM's at critical conditions. The CTA161 is designed to work at lower shear rates and to provide shear thickening which thus explains the observed difference in blade pressure before and after the trial. This is thus in agreement with results reported earlier[4] revealing to the behaviour of unstable rheological operating window.

For the various coating colours, the Brookfield Viscosity (100 RPM) was approximately the same (1180-1328 mPas) and so were the static water retention values (133-156 g/m²). Nevertheless, remarkable differences in behavior of the blade coater runnability were observed, i.e. referring to blade pressures. Differences in rheological and water retention behavior of these and other coatings have been presented in detail earlier[4].

**Figure 1A**

**Difference in blade pressure measured at the start and end of the trial**

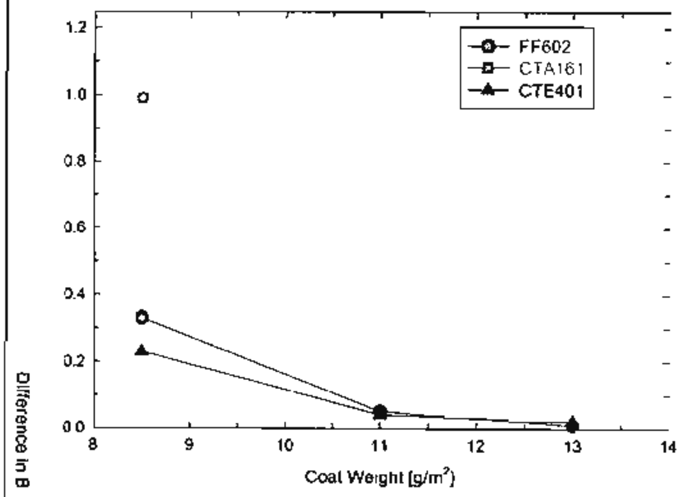
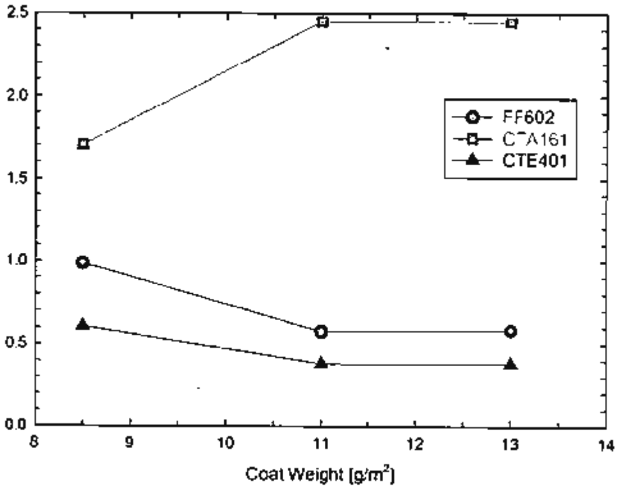


**Figure 1B**

**Average blade pressure measured during the trial**



**Note:** In Figures 1A and 1B, the blade angle for the coating colour containing CTA161 was changed from 42° to 22°; consequently the blade pressure is higher at the higher coatweights!

Recently, it was also presented that the chemistry of the WRRM's can control the macroscopic coating structure, in tablets made from coating colours[5]. It was found that the proper use of WRRM's can avoid defects in this structure such as air bubbles or latex depletion. The ToF-SIMS images of the tablets made from the coating formulations described in Table 1 are presented in *Figure 2*. The ToF SIMS images indicated that the differences in WRRM chemistry caused latex depletion and segregation to the surface.

Scanning Electron Microscope image analysis for the coated papers demonstrates semi-qualitatively the latex concentrations and uniformity on the coated surface, as presented in *Figure 2*. Image analysis reveals relative latex content on the surfaces from 4.9 to ~7% (area). This is less than earlier reported as concluded from ESCA analysis[11]. ATR-IR method has recently showed to be an efficient method for determination of latex content and mapping, while it was concluded that this method reports 1-2 parts lower latex contents than added. In the same study, however, it was reported that the latex content determined with SEM is lower than the addition level due to the particular analyzing procedure. It was also stressed that the small areas of latex cannot be identified with SEM[13]. Therefore, the SEM images presented here can also be regarded as an inverse measure of latex aggregation at the surface since very uniform latex content will likely not appear obvious in the analysis. In such case, it implies that there is a correlation between the qualitative ToF-SIMS images and SEM images.

Presented in *Figures 4 and 5* are the images from the X-Y plane of the coating and the qualitative analysis to calculate the % area covered by pigment, latex and air (or pores) respectively. Although the limitations of the SEM method as discussed elsewhere[13] it appears that the WRRMS causes clear differences in the surface morphology of the coatings.

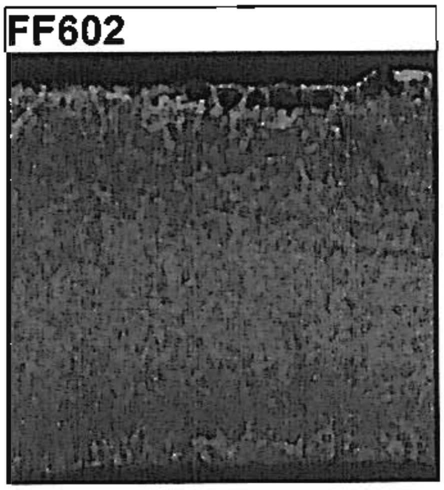


Figure 2

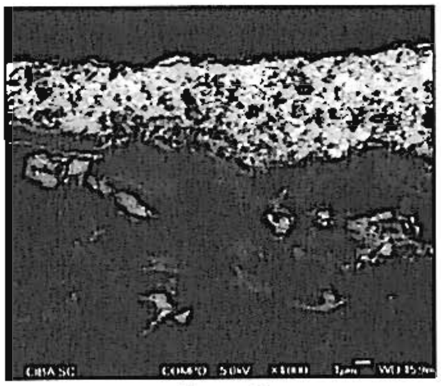


Figure 3

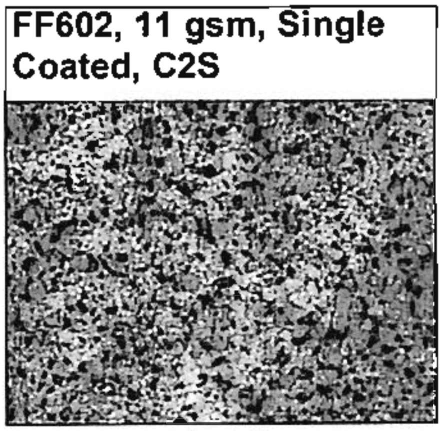


Figure 4

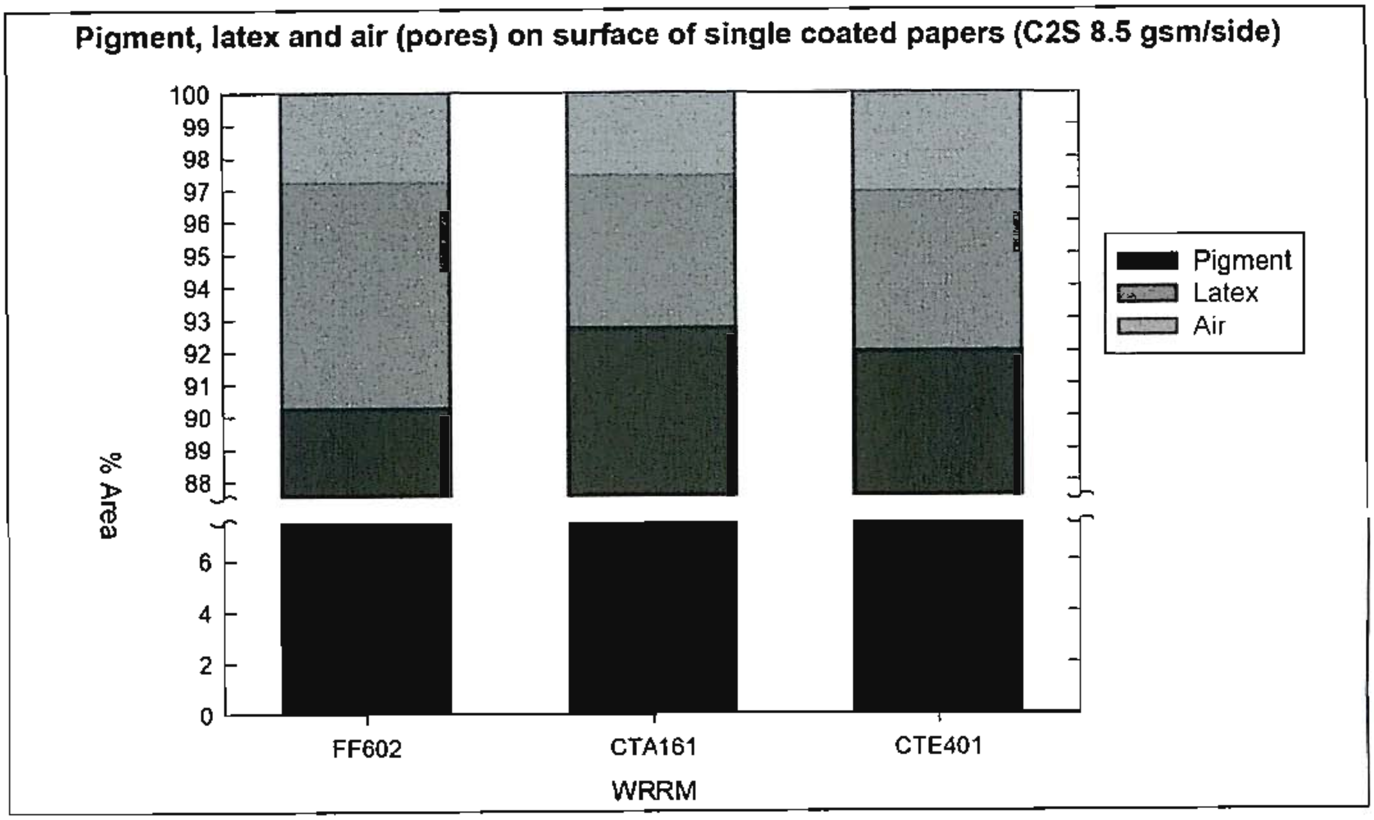


Figure 5

Presented in *Figure 6* are plots of uncalendered and calendared coated paper roughness (Parker Print Surf @ 10 kgf) as a function of coatweight. It is interesting to note the effect of WRRM's on the coating structure and especially on the surface roughness after calendering. Increased difference in roughness before and after calendering for papers with lower coat weight might in this case indicate different base paper-coating layer interactions.

Nevertheless, the laboratory results are partially confirmed here especially observation related to mechanisms such as particle depletion and coating structure homogeneity. The effect of base paper and pilot coater conditions are not considered in the laboratory study which must be considered when evaluating the results and especially the dynamic conditions.

**Effect of WRRM's on surface morphology**

As was discussed in the previous section, surface structure and particularly uniformity of the coated sheet can be affected by the WRRM chemistry, other than the obvious dosage and synergistic effects. While the primary intention of choosing a WRRM in a paper coating formulation might be to ensure coater runnability and uniform paper quality, secondary effects like impact on binder distribution must be considered[5],[13]. As demonstrated in several studies[2],[19], the binders might be tailored for controlled absorptivity of the structures.

*Figure 5* presents the weight % of pigment, latex and air (pores) on the coated paper surface for the sheets coated at 8.5 gsm per side (C2S). As discussed above, it indicates that the relative ratios of the 3 ingredients on the coated surface may be varied. In case of the organic component, correlations with the ToF-SIMS images are seen. Thus, we note an affirmation of the phenomenon of latex surface segregation, from two independent tests, viz., tablets and pilot coated paper.

Another manifestation of the surface morphology of the coated paper is presented in *Figure 6*. The surface roughness of the coated sheets through Parker Print Surf (10 kgf) measurements are presented as a function of the coatweight, for both calendared and uncalendared samples. At the higher coatweights, we note differences in roughness of the uncalendered samples. However, after calendaring, the differences are not significant any more. It is obvious that the uncalendered samples are more influenced by the base paper and the coating structure, whereas calendaring may smoothen out those differences.

An obvious effect of the surface morphology and coating structure is its effect on printability. In this study we restrict our analysis to the thickness of the ink film applied on a printing machine, while targeting the same print density. The ink layer thickness of sheetfed ink applied on the coated sheet, at the same ink density, was studied for some selected samples using

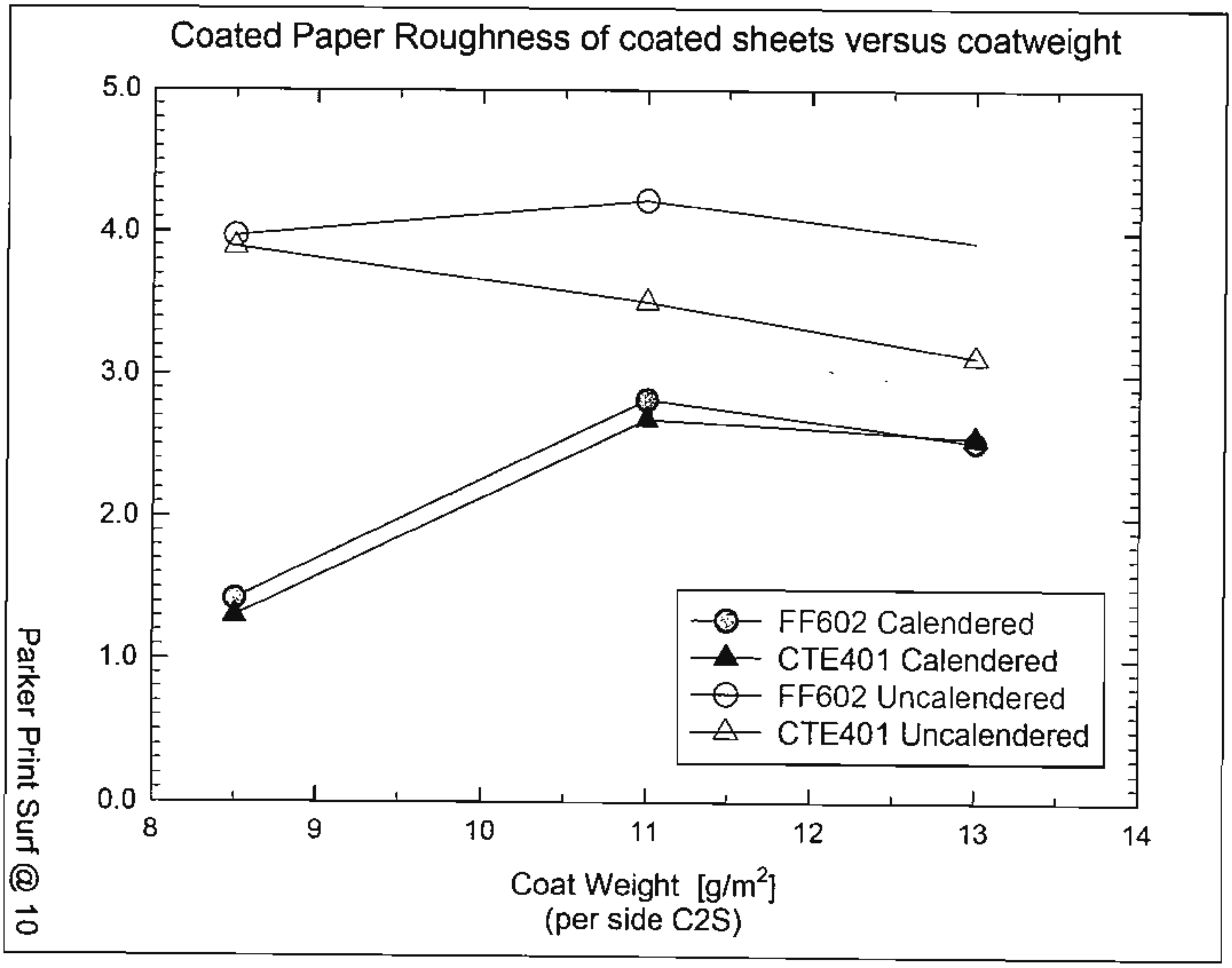


Figure 6

light microscope for imaging of cross sections. Results were calculated using analySIS 5.0 software of 10 parallel images. The method is summarized in *Figure 7*. An average and a standard deviation was calculated for each sample. The data from this analysis was used to construct the graphs presented in *Figure 8 and 9* described below.

*Figure 8* presents the area % of latex on the coated sheet surface *(as shown in Figure 4)* versus Ink Film thickness. We focus on slow setting Cyan ink only. The other inks showed identical trends and are therefore not discussed here. It indicates that the WRRM's can be also considered to control the distribution and surface concentration of the latex which directly impact on the ink uptake or causes a blocking effect. Since same ink density was targeted in this case, it appears that the ink film thickness reduces with increased latex concentration in the surface derived from SEM analysis, which thus is in agreement with statements made earlier[6][7][8][12]. The WRRM's may also be assumed to segregate to surface but its impact on ink film thickness is most likely limited.

In addition to differences in coating structure and surface morphology, of the structure, it is revealed that the local distribution of components clearly affects the interaction with the printing ink[7]. It appears that there is a negative correlation between the ink film thickness and latex concentration on the coated paper surface. A similar negative trend for the ink, printed both with and without water. This correlation implies a lower in ink film thickness with increased latex concentration at the surface when targeting same print density. Thus, to obtain the same print density, one needs less thick ink film when there is more latex on the coated sheet surface which suggests that latex fills the voids and thus reduces ink absorption[9]. Since the PPS roughness of the calendared sheets were similar, as shown in *Figure 6*, we can assume that PPS roughness had a minor impact.

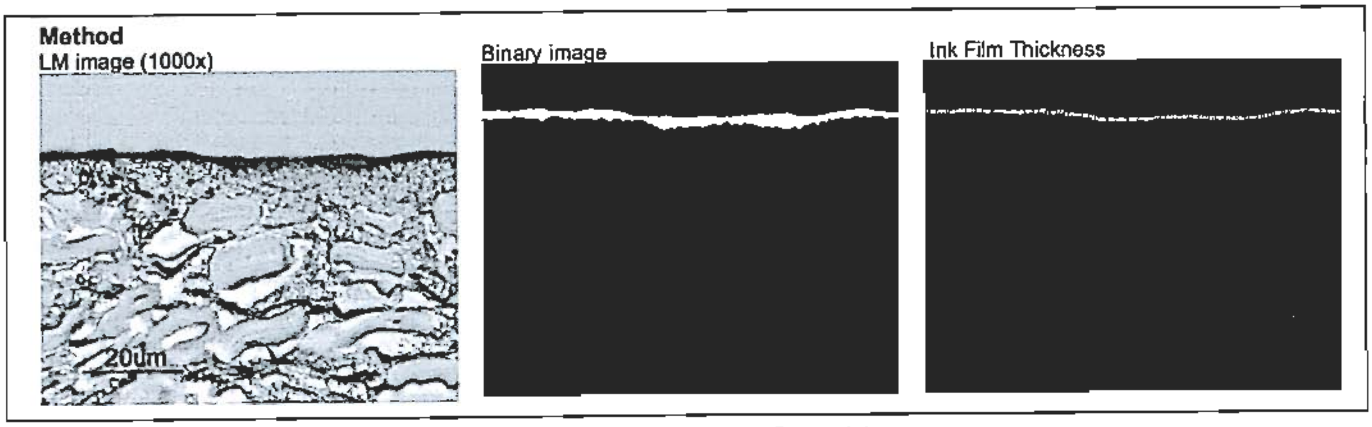


Figure 7 Determination of Ink Film thickness

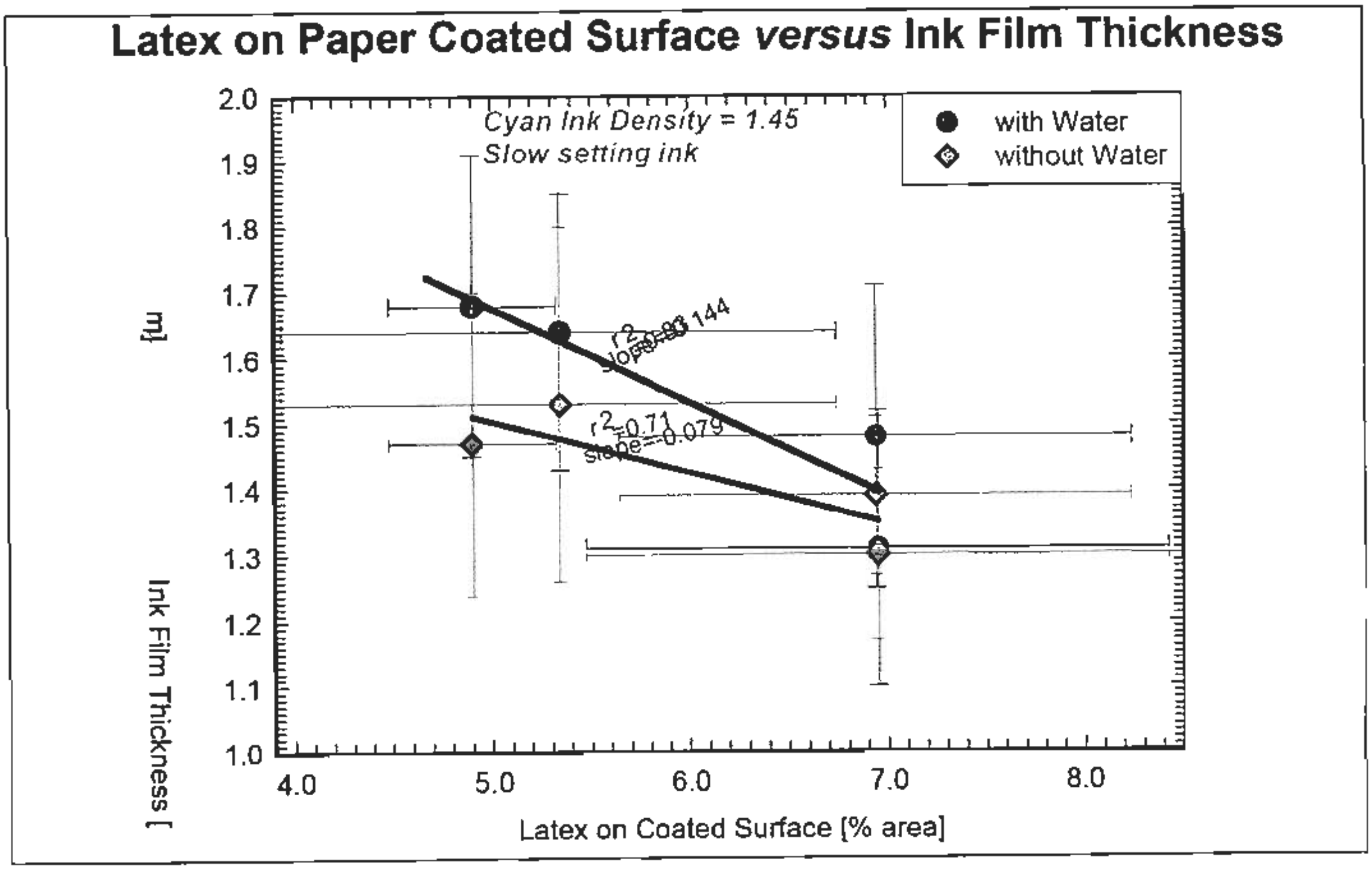


Figure 8

*Figure 9* presents the ink film thickness as a function of % air on the surface of the coated sheet, again obtained from the images presented in *Figure 4*. Here we note a positive trend, viz., higher porosity of the coated paper substrate the higher ink thickness to obtain the same ink density. This is intuitively obvious because higher porosity of the substrate would mean that more ink goes into the sheet and therefore less of it is available to contribute to higher ink density. Since porosity was not a primary focus of this study, further analysis was not attempted.

## Conclusions

We present a study on the effect of WRRM chemistry on the coating structure.

We have demonstrated the distribution of latex along the Z-direction of the coating layer and on the plane, which is controlled primarily through the choice of the WRRM. A semi-qualitative agreement between the Z-direction latex uniformity found in the laboratory made tablets and the coating layer of pilot coater coated sheets was observed.

It is also concluded that uniformity of the latex distribution, influenced by the WRRM chemistry, induces noteable effects on the surface morphology of the coated sheets. The coated sheets, which were printed on a commercial offset sheetfed printer, revealed different ink layer thickness which was ascribed to the characteristic surface morphology of the coatings.

Thus, surface topography with specific functionality can be controlled via controlled interactions in the suspension and structure build-up. New polymer technology provides unique solutions to increase water retention behavior of the WRRM, but these can be further used to adjust final coating structure such as optical properties or print quality.

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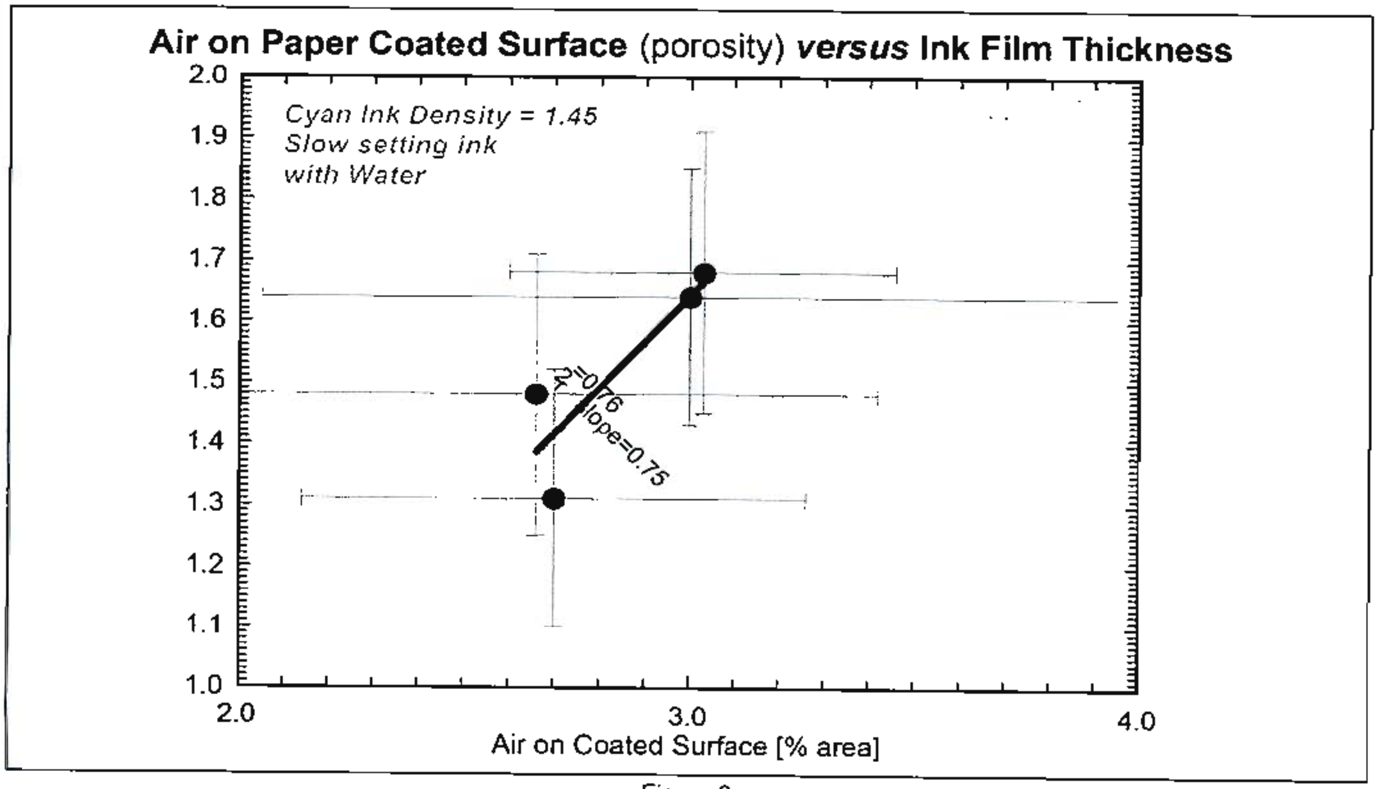

Figure 9

# NOTES

# Material Retention: A Novel Approach to Performance of Pigment Coating Colours

by
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CP Kelco Oy

SESSION THREE
PAPER FOURTEEN

## Abstract

Cost efficiency is today the primary requirement in the paper and board industry. This has led therefore, to a greater preponderance of products with specifically designed functionality to take account of current industry needs. Continually increasing machine coating speeds together with these new coating colour components have put more emphasis on the importance of the correct rheology and water retention of the coating colours to achieve good runnability and end product quality.

In the coating process, some penetration of the aqueous phase, to the base paper or board must occur to anchor the precoating to the base or the topcoat to the pre-coat. The aqueous phase acts as a vehicle not only for the binder, but also for the other components. If this water or material penetration is not controlled, there will be excessive material shift from the coating colour to the base, before immobilization of the coating colour will stop this migration. This can result in poor machine runnability, unstable system and uneven coating layer, impacting print quality.

The performance of rheology modifiers or thickeners on the coating colour have tended to be evaluated by the term, "water retention". This simple term is not sufficient to explain their performance changes during coating. In this paper we are introducing a new concept of "material retention", which takes note of the total composition of the coating colour material and therefore goes beyond the concept of only water retention. Controlled material retention leads to a more uniform z-directional distribution of coating colour components. The changes that can be made to z-directional uniformity will have positive effects on print quality as measured by surface strength, ink setting properties, print gloss, mottling tendency. Optical properties, such as light scattering, whiteness and light fastness delivery should also be improved. Additionally, controlled material retention minimizes changes to the coating colour with time in re-circulation giving less fluctuation in quality in the machine direction since it more closely resembles fresh coating for longer periods.

Use of the material retention concept enables paper and board producers to have more stable runnability (i.e. lower process costs), improved end product quality (i.e. better performance of used chemicals) and/or optimized use of coating colour components (i.e. lower total formulation cost).

## Summary of Results

As stated earlier, controlled material retention has a target of ensuring that the coating colour remains stable throughout the process and to control the mobility of the material in the coating layer prior to immobilization. Once both of these targets are reached the end product quality is more uniform both in machine and z-direction. Key observations from our work can be summarized as follows

- Controlled material mobility ensures uniform end product quality such as surface strength and whiteness.
- Blade induced pressure penetration is more significant with jet application compared to roll application and therefore understanding and control of the particle mobility under higher shear rates becomes more critical.
- The understanding of the influence of thickeners (and the mechanism of slip velocity) on the boundary layer is highly important in assessing their impact on machine runnability and end product quality.
- Penetration of material through excessive particle mobility can be controlled through modification of aqueous phase viscosity and immobilization properties.
- Insufficient control of material retention results in changes in the particle size distribution of the coating colour. This leads to deviations in the colour due to re-circulation of coating colour thus negatively impacting machine direction quality uniformity.

## Introduction

Cost efficiency is today the primary requirement in the paper and board industry. Cost efficiency means maximized productivity (good runnability, minimum amount of broke - stable process) and optimized use of raw materials (maximum performance with minimum addition level - right component in right place) resulting in uniform end product quality. This has led therefore, to a greater preponderance of products with specifically designed functionality to take account of current industry needs. For example the development of the pigments and the latexes has a similar trend; smaller particles and narrower particle size distribution. Continually increasing coating machine speeds together with new or modified coating colour components have put more emphasis on the importance of the correct rheology and water retention of the coating colours to achieve good runnability and end product quality. Today the coating colour optimization is often done on a single component basis, but in order to be truly cost efficient, a more holistic view should be taken to ensure coating colour optimization.

The aqueous phase of the coating colour acts as a vehicle for its various components. If this water (and material) penetration is not controlled, there will be excessive material shift from the coating colour to the base, before immobilization of the coating colour will stop it. The migration rate towards the surfaces of primarily pigment particles, latex and OBA will have a significant impact on coated paper quality and machine runnability. This migration rate is exacerbated particularly if especially small size and narrow distributions of pigment and latex particles are used. This results in a greater rate of mobility, significantly influencing particle-packing behaviour and resultant end product quality.

In this paper we will demonstrate that it is possible to control mobility of the material by the correct choice of a thickener. This will be illustrated by end product performances such as surface strength, optical and printed paper properties showing the impacts of thickener type on the perceived improvements to z-directional distribution of the materials. Furthermore we will show that material retention can be evaluated and a predictive assessment to mill scale performance be made by indirect methods in laboratory scale. This will be of great benefit and importance to coating mills for cost effective performance of their coating units. This is achieved through the optimization of the location of the key coating components throughout the coating layer to maximize their performance. Traditionally coating colour research concentrates on fresh coating colour analysis. The results therefore, can be contradictory to mill scale findings as the stress factor of coating colour processing is missing, severely minimizing the value of the obtained results.

Historically, indirect methods such as low and high shear viscosity and static water retention have been utilized to evaluate coating colour performance and in many cases still are. These methods seldom take into account the influence of key factors such as base paper, coating colour circulation or coating process stabilization time. In order to achieve a more complete picture of the influence of coating dynamics, we have adapted known test methodologies, namely dynamic water retention (DWR), slip velocity and particle size distribution of coating colour to allow this. The combination of these methods allows us to monitor changes in coating colours during the coating process and suggest formulation modifications to maximize performance.(1)

In this paper four different coating colours were adjusted from the perspective of improved material retention according to the findings published in our previous paper(1) of the methods developed. Paper coating, calendering and printing were done on pilot scale, the details of which are summarized later in this paper. Three different co-binding/thickening systems were chosen to assess their impact on effective control of material movement and thus z-directional distribution. Additionally, one further formulation with a lower latex level with a modified CMC was run to determine the impact on binder mobility, since there are obvious cost in use implications if successful. The pigments, additives and coating colour solids were kept constant. High shear viscosities were adjusted to the level that is considered appropriate for good runnability, by adjustment of the co-binding/thickening component. From experience this is targeted at 35 - 50 mPa·s using a capillary rheometer. The slip velocity can be used to assess the mobility of aqueous phase at high shear rates, and was adjusted to the level below 10 m/s (at 17,000 $N/m^2$), which under these conditions we have found to be suitable in the efficient control of material mobility.

## Mobility of the aqueous phase

When coating colour is applied onto the paper, there is a natural penetration of the aqueous phase into the paper influenced by, the coating colour characteristics, by the base paper properties and the type of coater application/metering geometry. The aqueous phase contains pigment fines, binders, optical brightener, water soluble materials and free dispersing agents. It is therefore evident that the ability to control the mobility of these functional components are critical to ensure optimum machine performance and end product quality and uniformity.

In the blade coating process, the aqueous phase penetrates into the paper by both capillary and pressure forces. Pressure penetration is facilitated during coating application and under the blade during the metering phase. Base sheet penetration through capillary action, happens in the phases between coating application and blade metering and in the subsequent period until total coating immobilization occurs. Quantitatively it is difficult to separate out these two types of penetration, since both phenomena occur at same time regarding liquid penetration into the paper. It has been demonstrated(2,3) that pressure has a fundamentally more important influence on liquid penetration than contact time. It is important therefore to keep this in mind in relation to continuing increases of coater speed.

Capillary and pressure penetration relate to different characteristics of the coating colour. The wetting ability of the aqueous phase on wet pigments and on wet fibres has significance. If the aqueous phase wets fibres well, but doesn't wet pigments, both capillary and pressure penetration are high. The pigments adsorb different amount of water; clay more than calcium carbonate and fine pigments more than coarse. However under external pressure the pigment particles come closer to each other and they will lose some adsorbed water. Consequently the balance of surface energies and polarity of different components control both the penetration rate and level. Increased solids of the coating colour at constant coat weight necessitates higher blade pressures, thus increasing the pressure penetration.

Increase in aqueous phase viscosity slows down penetration. Temperature has an influence on the penetration via the impact on aqueous phase viscosity. At high temperature the viscosity is lowered and the resulting penetration is greater. If the binder/co-binder is poorly adsorbed on the pigment, or bonds break down under pressure/shear forces, more binder remains in the aqueous phase and the resultant viscosity of the aqueous phase will increase through the different mechanisms described later in this paper.(4,5)

There are several factors relating to the base paper, which also have influence on the amount of absorbed liquid. It has however been shown that modifications of colour have a greater influence on the penetration tendency of the aqueous phase, than changes in the absorption characteristics of base paper.(6)

In jet applications, a significantly lower pressure pulse prior to blade tip is applied on the coating compared to roll application resulting in a significantly thinner filter cake and a lower penetration of materials. A thinner filter cake before the blade is also the reason for a slightly higher dewatering under the blade. The highest pressure occurs under the blade tip,(7) so it can be assumed that from a material penetration point of view in jet applications the role of blade load is greater than in roll applications. At higher speed the dwell time prior the blade becomes shorter and an even thinner filter cake is formed before the blade. Due to this the pressure penetration and dewatering tendency increases and the material flow control becomes even more critical, again impacting machine performance and end product quality.

## Experimental

### Thickeners

This work covered different types of commercial thickeners, which have different thickening mechanisms, resulting in different kinetic impacts on water and material retention. One of the thickeners was a conventional sodium carboxymethyl cellulose (CMC) used in paper coatings. Another thickener was a modified CMC, where the cellulosic backbone has been manipulated during the manufacturing process to provide improved material retention properties through enhanced water retention capability and faster immobilization through improved associative behaviour(1). A further test point was an alkali swellable emulsion (ASE). Low molecular weight fully hydrolyzed polyvinyl alcohol was used in conjunction with the ASE synthetic. This is a typical industry practice to provide additional properties, which synthetics in general do not normally provide alone.

Water-soluble rheology modifiers impart their effect on a system through one or more distinct mechanisms. The thickening mechanism is strongly related to the chemical structure of the chosen rheological additives. The main types of mechanisms for thickeners when building their viscosity are presented in *Table I*.

### Base paper

The base paper used in the trials was pre coated un-sized wood free paper. The pre coat weight was 8 $g/m^2$ and the total grammage 91 $g/m^2$.

### Coating formulations

Coating formulations used in this work consisted of the following:

- Narrow particle size ground calcium carbonate
- Fine china clay
- Carboxymethyl cellulose (Finnfix CMC)
- Typical alkali swellable emulsion
- Small particle size SB-latex
- Low molecular weight fully hydrolyzed polyvinyl alcohol
- Tetra sulfonated optical brightening agent

Formulation details are listed in *Table II*.

Coating colours were made to constant solids content at pH 8.5 and 9. The latex level in one coating colour using the modified CMC grade was decreased by one part in order to assess the effect of this specific product on the z-directional distribution of binder.

| | Conventional CMC | Modified CMC | ASE | PVOH |
|---|---|---|---|---|
| Associativity | +* | ++* | + | +* |
| Aqueous phase viscosity | +++ | +++ | ++ | + |
| * = Depending on the pigment system | | | | |

Table I. Main mechanisms types for thickeners

| Colour | Conventional CMC | Modified CMC | Modified CMC + less latex | ASE + PVOH |
|---|---|---|---|---|
| GCC | 70 | 70 | 70 | 70 |
| Clay | 30 | 30 | 30 | 30 |
| CMC | 0.7 | 0.6 | 0.7 | - |
| PVOH | - | - | - | 0.4 |
| Latex | 10 | 10 | 9 | 10 |
| OBA | 0.5 | 0.5 | 0.5 | 0.5 |
| Synthetic thickener | - | - | - | 0.3 |
| | | | | |
| Solids, % | 63 | 63 | 63 | 63 |
| pH | 8.5 | 8.5 | 8.5 | 9.0 |

Table II. Coating colour formulations

### Pilot data

Pilot trials were carried out at KCL (Keskuslaboratorio Oy, Finland). The essential trial conditions are presented in *Tables III, IV and V.*

The target moisture content was 5.0 %. The base paper was heated using electrically powered infra drier. The coated papers were dried using electrically powered infra driers and gas heated airfoil driers.

### Coating colour analysis

Basic properties of coating colours (solids content, pH, static water retention, density and viscosity at different shear rates) were analyzed. Solids content was measured with Mettler-Toledo HR73 Halogen moisture analyzer. Viscosities of coating colours were measured with Brookfield RVDV-II+ viscometer (100 rpm), Hercules HI-shear viscometer DV-10 and with capillary rheometer (DT Paper Science) (capillary: 50 mm/0.5 mm). Static water retention (ÅA-GWR) was measured using constant coating colour volume 10 ml (5 °m membrane, 0.3 bar pressure, 2 min). Density was measured gravimetrically. Furthermore slip velocity was measured with capillary rheometer (DT Paper Science)(8), dynamic water retention was determined with coater by DT Paper Science applying Novicoater method(1) and the particle size distribution was analyzed using Coulter LS 13 320MW device. All measurements were performed after standardized handling at constant temperature (25°C).

### Coated and printed paper analysis

Standard paper analyses were performed to coated papers. In this paper we are presenting the results that are relevant from the material retention point of view. To these critical parameters were chosen surface strength, CIE-whiteness and print gloss.

Surface strength was measured with IGT AIC2-5 according ISO 3783 standard. CIE-whiteness was measured with Minolta CM 3700D according ISO 11475 standard. From 4-colour printed papers print gloss (90 % black, 67 % cyan, 67 % magenta and 67 % yellow) was measured with Hunter 75°.

## Results

### Coating colours

*Viscosities*

Properties of the fresh coating colours are presented in *Table VI.* There were differences in viscosities at different shear rates of coating colours since thickener dosages were selected in order that mobility of the aqueous phase was controlled. Coating colours with CMC as thickener had similar viscosities through the whole measured shear rate area. Coating colour with synthetic thickener had lower Brookfield viscosities and higher high shear viscosities that CMC colours. The viscosities at high shear rates are presented in *Figure 1.*

| Colour | Conventional CMC | Modified CMC | Modified CMC + less latex | ASE + PVOH |
|---|---|---|---|---|
| Speed, m/min | 1200 and 1500 | 1200 and 1500 | 1200 and 1500 | 1200 and 1500 |
| Beam angle, ° | 50 | 50 | 50 | 50 |
| Blade dimensions | 0.381/84 mm, 40° | 0.381/84 mm, 40° | 0.381/84 mm, 40° | 0.381/84 mm, 40° |
| Pumping speed, % | 45 | 35 | 35 | 35 |
| Blade pressure, bar (1200 m/min) | 0.63 | 0.58 | 0.57 | 0.66 |

Table III. Coating conditions (Opticoat Jet-coating)

| | All trial points |
|---|---|
| Nips | 4+1+5 |
| Temperature °C | 70 |
| Speed, m/min | 750 |
| Target gloss % | 70 |

Table IV. Supercalendering conditions (Multical)

| | All trial points |
|---|---|
| Speed, sheet/h | 5000 |
| Printing inks | Rapida series (HostmannSteinberg) |
| Target densities | black 1.85, cyan 1.50, magenta 1.15, yellow 1.15 |

Table V. Printing conditions (Roland Favorit RVF)

| Fresh coating colour | Conventional CMC | Modified CMC | Modified CMC + less latex | ASE + PVOH |
|---|---|---|---|---|
| Solids, % | 63.1 | 62.8 | 62.8 | 63.2 |
| Density, kg/dm³ | 1.47 | 1.45 | 1.45 | 1.44 |
| Static water retention ÅA-GWR, g/m² | 145 | 150 | 135 | 125 |
| BrRV viscosity (at 100 rpm), mPa·s | 1400 | 1200 | 1300 | 750 |

Table VI. Properties of fresh coating colours

Properties of the coating colours after the pilot trial are presented in *Table VII.* Minor changes in basic properties were noticed and only major change happened in the density of the synthetic thickener coating colour; density decreased about 8% during the trial due to air entrapment. All coating colours were diluted slightly due to edge showers.

*Water retention*

The static water retention method (ÅA-GWR) is a measure of the amount of water released from the coating colour during a certain time under a defined pressure. The greater the value the worse the apparent water retention under these static conditions.

The dynamic water retention method (Novicoater DWR) is based on the actual change of the coating colour solids during the coating process. The lower the change in solids content of the coating colour, the better the water retention.(1) Although the static method results indicate that synthetic thickener coating colour has better water retention, there is virtually no differences in the results measured at dynamic conditions *(see Figure 2.)* Based on our previous experiences we can see that all the coating colours have good water retention, which combined with correct high shear viscosity levels is beneficial for good runnability. The differences seen here are not significant and is a further confirmation that our methods allow more targeted control of mobility.

*Slip velocity*

Slip is an inherent characteristic of a pigmented coating suspension that depends on pigment particle packing behavior and solids fraction volume; the state of dispersion and the flowability of the continuous phase and is measured using capillary viscometry. A possible mechanism for the creation of a slip layer is a lower concentration of particles next to the capillary wall than in the bulk colour, due to the particle migration and size segregation. These phenomena have been detected during shear flow with several optical methods and analyzed mathematically. The slip layer has a relatively high shear velocity and more material flows through the capillary tube than expected by theory with non-slip boundary conditions. Slip velocity can be related to easy release of water from the bulk colour, lubrication ability of small particles (ball bearing effect) or polymer coils (viscosity of aqueous phase).(8)

It is essential to understand the control mechanism of the material mobility so that to the correct level of slip velocity can

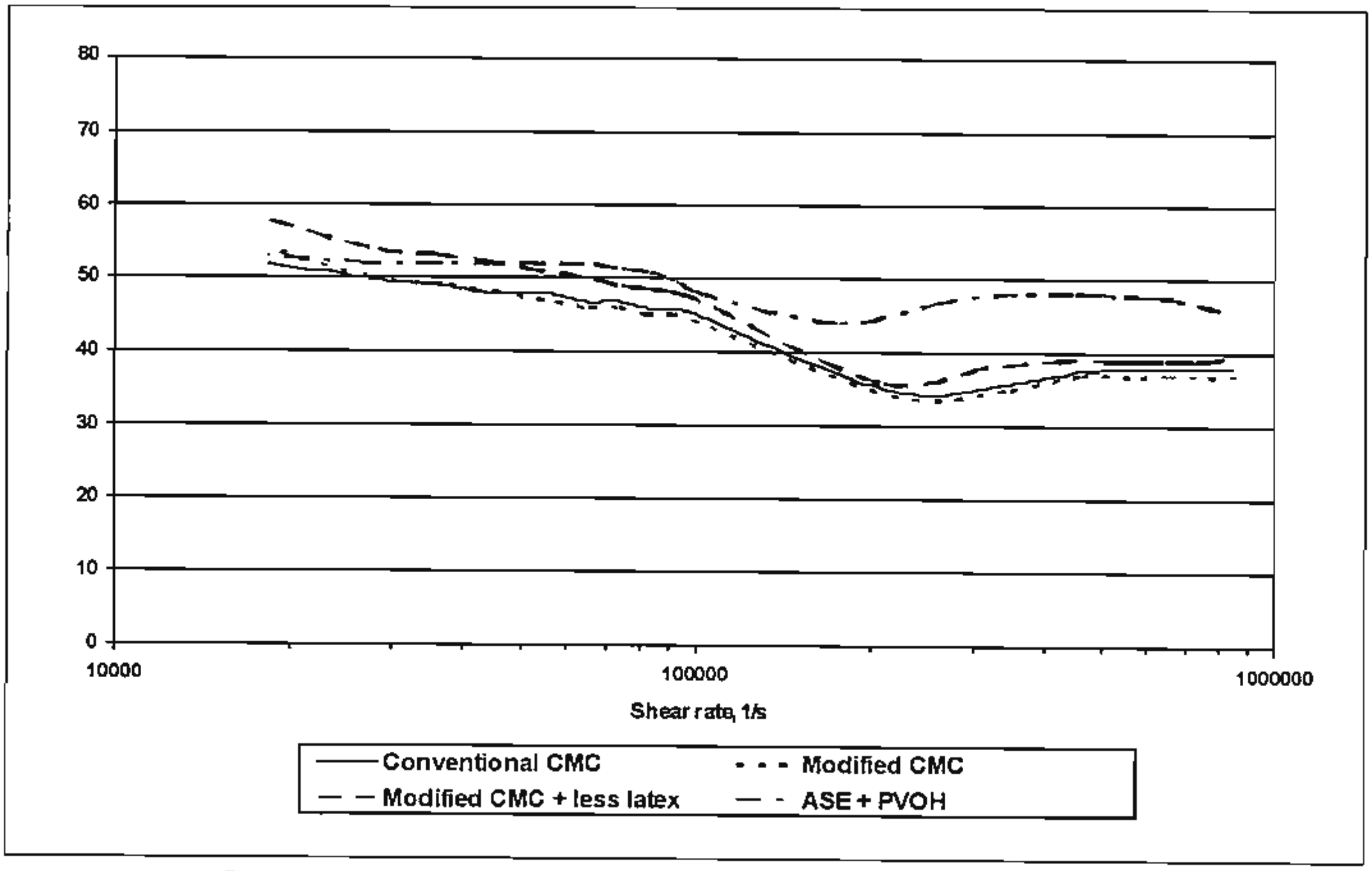


Figure 1. High shear viscosity curves of fresh coating colours (Hercules + capillary).

| After trial | Conventional CMC | Modified CMC | Modified CMC + less latex | ASE + PVOH |
|---|---|---|---|---|
| Solids, % | 62.8 | 62.5 | 62.5 | 63.0 |
| Density, $kg/dm^3$ | 1.45 | 1.40 | 1.41 | 1.32 |
| BrRV viscosity (at 100 rpm), mPa·s | 1300 | 1200 | 1300 | 750 |

Table VII. Properties of coating colours after pilot trial be determined. Thickener dosages in these coating colours were adjusted so that slip velocity of all coating colours was on a low level, which under these conditions is correct in order to control the material mobility efficiently. Slip velocities did not change significantly during the pilot trial coatings. Slip velocities of fresh coating colours are presented in *Figure 3*.

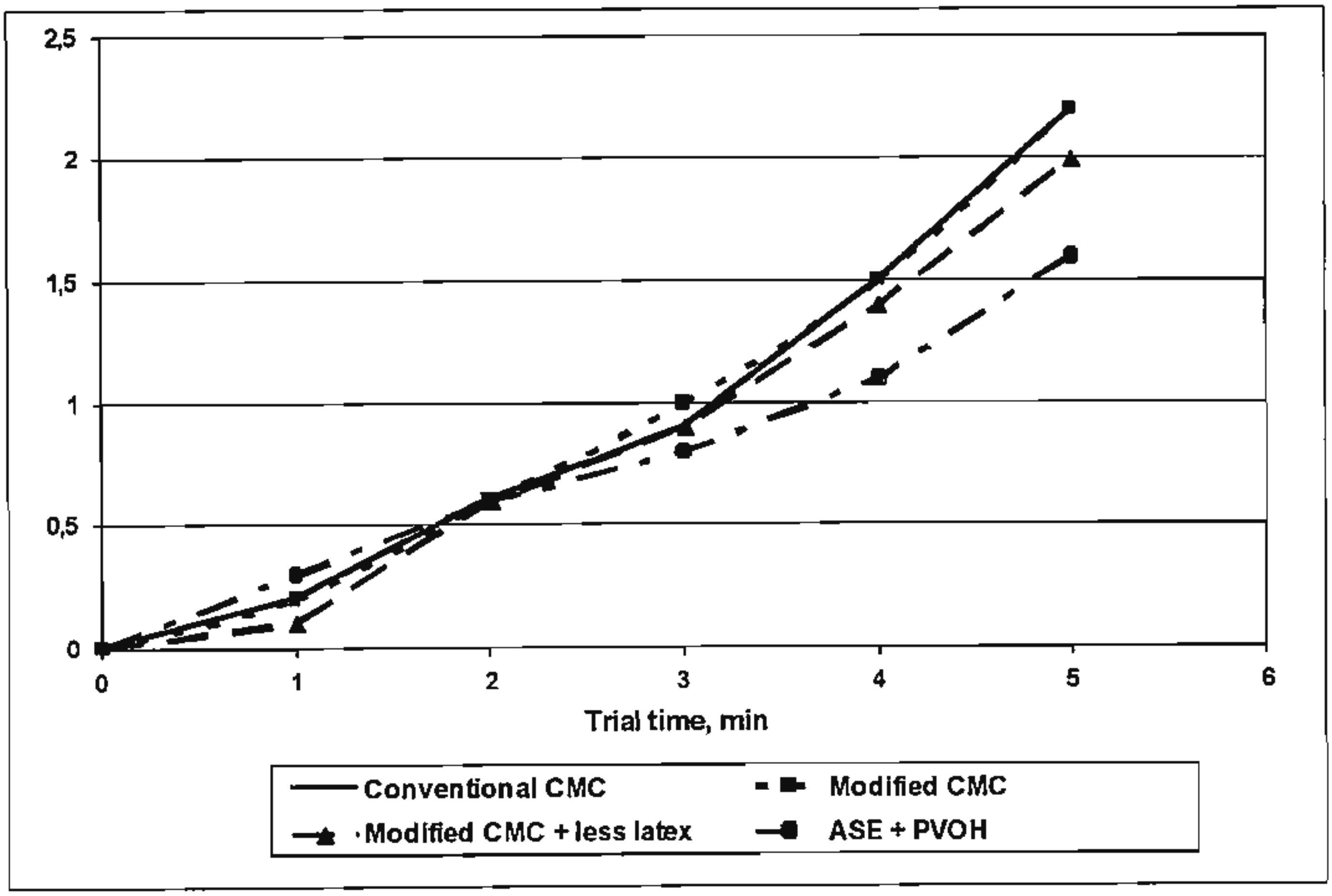


Figure 2. Dynamic water retention results of the fresh coating colours.

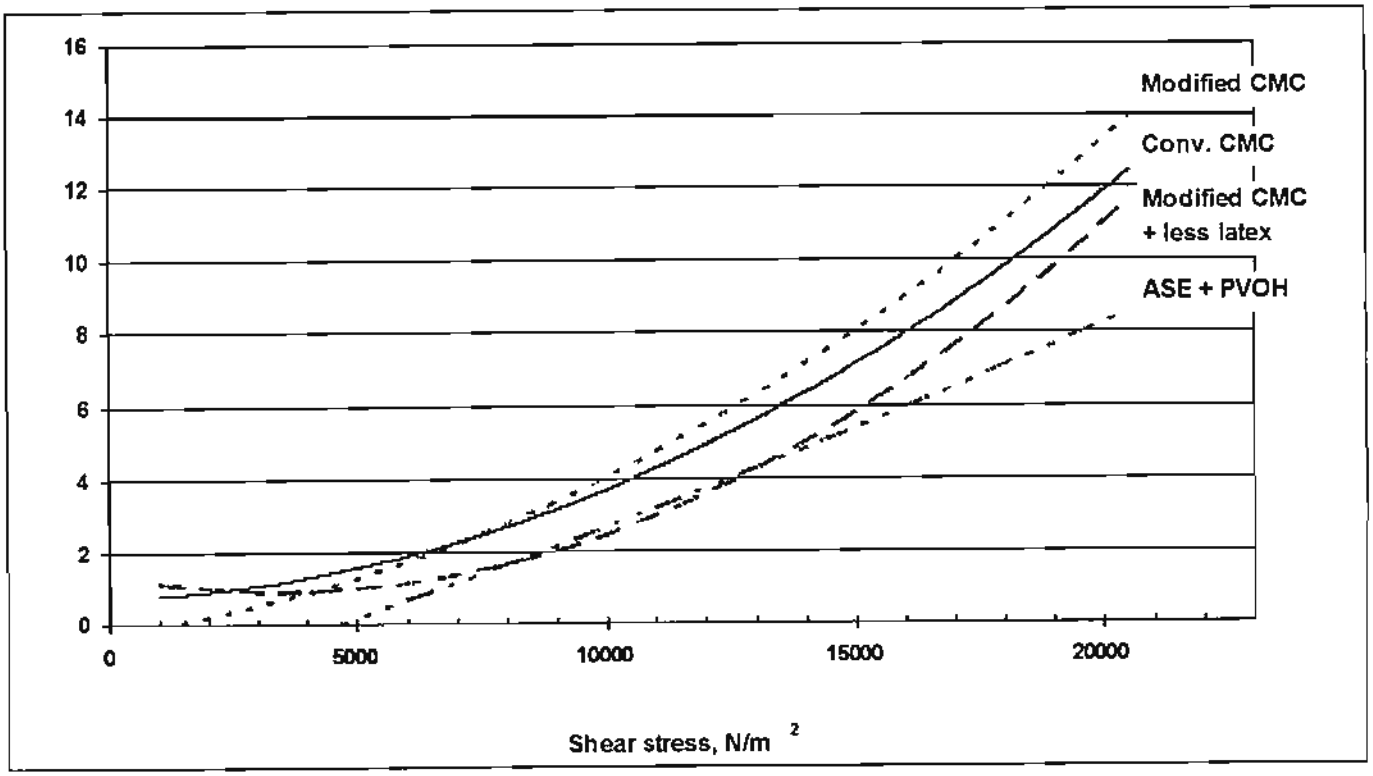


Figure 3. Slip velocity results of the fresh coating colours.

*Particle size distribution*

Coulter LS 13 320 particle size analyzer measures particle sizes with an assumption that all particles are round, and therefore it is not possible to get absolute particle sizes. However, studying the changes in particle size distributions is an effective way to monitor the stability of coating colours even if all particles are assumed to be round. The stability of coating colours can be monitored by measuring particle size distributions of fresh coating colours and coating colours after the run and by comparing particle size distributions to each other. Changes indicate phenomena such as coating colour homogeneity being compromised through excessive movement of particles of certain size (relatively in volume) or if aggregates are formed.

Particle size distributions of coating colours before and after the pilot trial coatings are presented in *Figure 4*. Coating colours with modified CMC were very stable and only small if any changes in particle size distributions could be seen during the pilot trial. Coating colours with traditional CMC or synthetic thickener/PVOH had some changes in particle size distributions during the trial even though the mobility of aqueous phase was controlled and therefore the mobility of particles should be restricted. This is most probably due to higher blade pressures required for these two coating colours. Higher blade pressure, as indicated earlier results in higher pressure penetration forces leading to preferential movement of coating colour components more towards the base paper. This leads to more difficult control of material movement. The reasons for higher blade pressures were higher capillary viscosity (synthetic thickener) and higher amount of coating colour applied to the paper due to higher flow rate of the jet (conventional CMC). To be able to control the movement of material with high blade pressure even more controlled material mobility is needed. Understanding the implications of this facilitates the correct choice of coating colour composition.

**Coated and printed papers**

Controlled material retention allows the coating colour to remain more stable throughout the process and to control the mobility of the material in coating layer prior to immobilization. Once both of these targets are reached the end product quality is much more uniform both in machine and z-direction. Coating colour testing give indications about the coating colour stability and therefore also about machine directional uniformity. Paper tests enable us to postulate the impact on z-directional uniformity.

*Surface strength*

Surface strength of the papers was determined by measurement of picking and delamination tendencies in the laboratory *(see Figure 5)*. These tests did not show any differences between the trial points. This indicates that significant reduction in binder level is possible if the material retention is properly controlled. The fact that CMC also functions as a

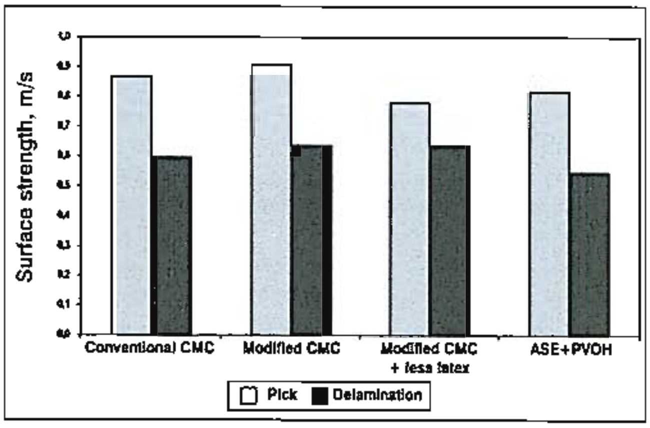
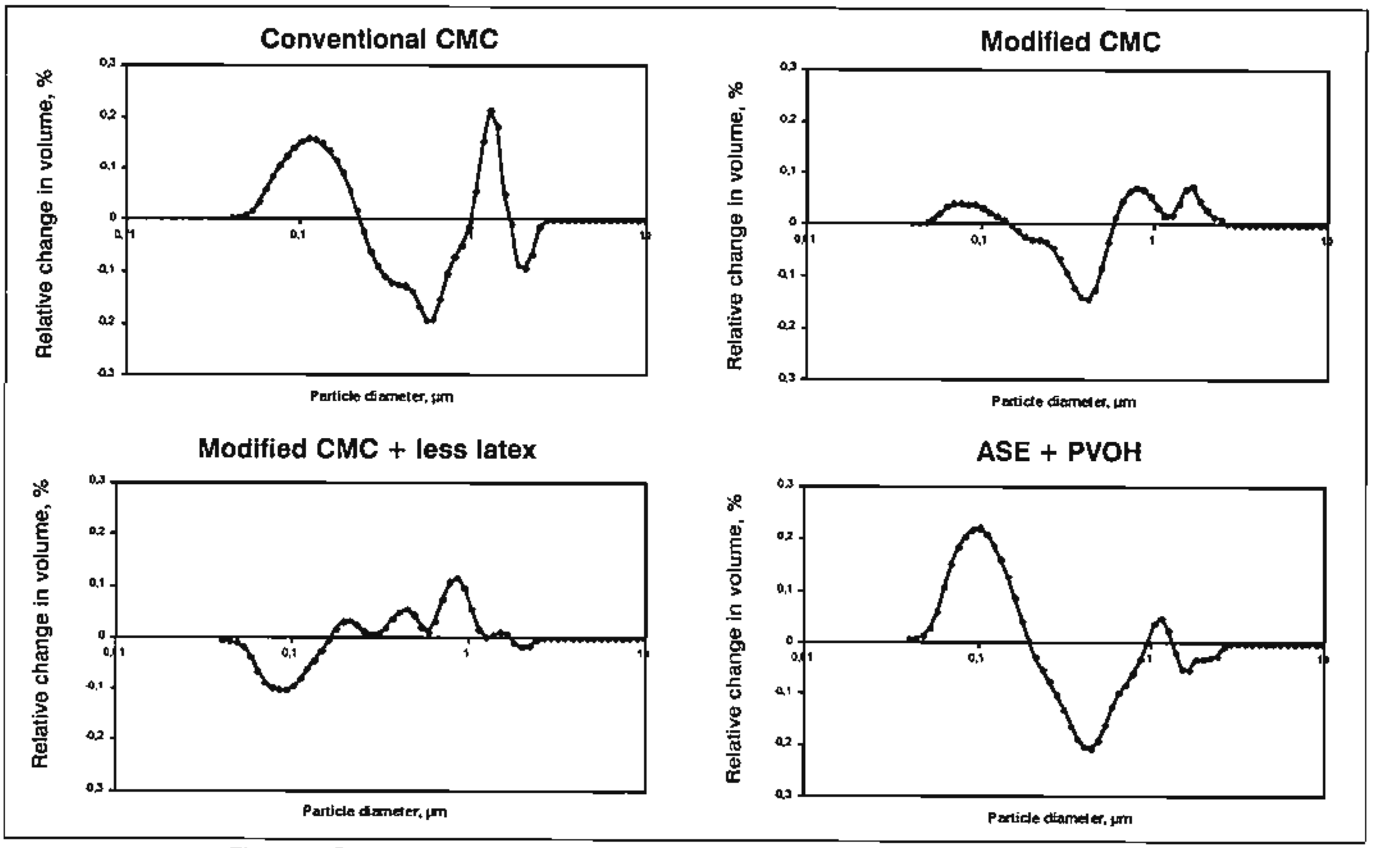


Figure 5. Surface strength (cd)


Conventional CMC

Modified CMC

Modified CMC + less latex

ASE + PVOH

Figure 4. Particle size distributions of coating colours before and after the pilot trial.

binder in its own right (binder strength higher than with SB-latex(9)) becomes more significant when lower latex levels are considered as part of cost reduction programs.

*CIE-whiteness*

CIE-whiteness was measured from the papers coated at 1200 m/min and 1500 m/min with equal coat weights (12 $g/m^2$). The results are presented in *Figure 6*. Changes in particle size distribution already indicated that there is more material movement in the synthetic thickener coating colour and the whiteness results are confirming this. Increased pressure penetration is most likely forcing material, particularly OBA more towards base paper and therefore resulting in lower whiteness level due to the location of the OBA. The difference is increasing with higher machine speed suggesting sub-optimal mobility control despite meeting slip and water retention targets.

*Print gloss*

In order to see the influence of co-binder systems on printability all the papers were calendered to the same gloss level. We have made the assumption that the papers have comparable micro smoothness levels as well. Print gloss results presented in *Figure 7* show that there are minor differences between the CMC coating colours. It is known that latex reduction will give a more porous surface impacting the printability. Correct choice of CMC grade and addition level together with controlled material retention ensures that there are no changes in end product printability. Meanwhile the synthetic thickener coating colour gives much lower print gloss. Variations in print gloss we believe are most probably due to differences in component composition on the surface (i.e. latex level) and in pore structure as evidenced by the changes in particle size distribution shown earlier. The air entrapment into the coating colour which can be a tendency of this system will also result in an even more porous surface structure.

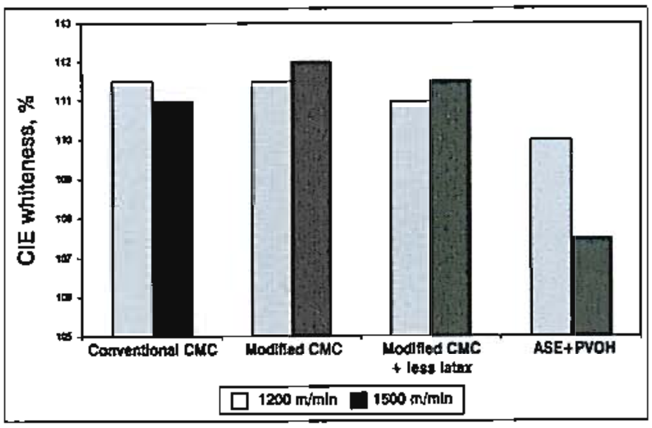


Figure 6. CIE-whiteness

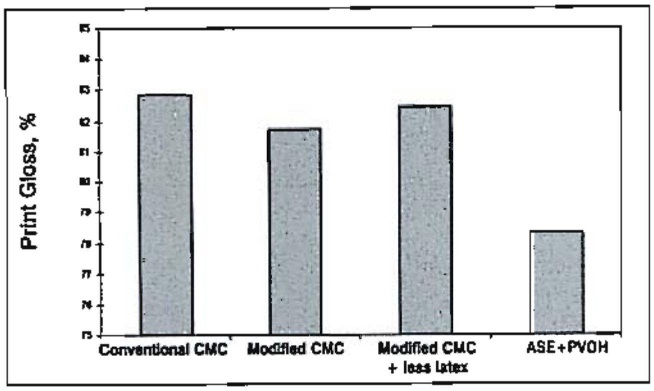


Figure 7. Print gloss

## Conclusions

This concept of material retention takes note of the total composition of the coating colour material and therefore goes beyond the concept of only water retention. In this paper four coating colours were optimized to have best possible material retention without sacrificing the runnability. Actual coating results showed that even minor differences in coating conditions can have significant impact on end product quality. Therefore it is even more important to have a holistic view on the whole coating process including base paper, coating colour and process parameters.

The material movement due to pressure and capillary penetration can be controlled by aqueous phase mobility, immobilization properties and high shear viscosity. It is important to have all these parameters on the correct level simultaneously. Traditional methods of coating colour measurement, such as low shear viscosity, static water retention are not sufficient for determining potential performance; they are suitable only for quality control purposes.

The slow immobilization of the conventional CMC coating colour combined with the high blade load led to higher material movement, which could be seen in changes in particle size distribution. Although there were no major changes seen in this study with the CMC colours, this could lead to changes in end product uniformity in machine direction in continuous operation. High capillary viscosity of the synthetic thickener coating colour led to blade load induced pressure penetration causing major changes in particle size distribution and lower end product quality even in this short trial. Therefore it can be concluded that it was not possible to optimize both capillary viscosity and aqueous phase mobility simultaneously. Modified CMC coating colours with controlled material retention gave the most uniform results. This enabled the optimization of the latex level without changes in surface strength and print gloss.

As a final conclusion, controlled material retention leads to more uniform z-directional distribution of coating colour components. Additionally, controlled material retention minimizes changes to the coating colour with time in re-circulation giving less fluctuation in quality in the machine direction since it more closely resembles fresh coating for longer periods. Use of the material retention concept enables paper and board producers to have more stable runnability (i.e. lower process costs), improved end product quality (i.e. better performance of used chemicals) and/or optimized use of coating colour components (i.e. lower total formulation cost).

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# Today's Trends in Coating Kitchens, Supply Systems and Coating Effluent Treatment

*by*
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SESSION THREE
PAPER FIFTEEN

## Abstract

Basic coating colour preparation systems have remained quite similar in design concept for many years. The demand for proven reliability, together with characteristic paper industry conservatism has prevented overly "radical" solutions from entering the market. However there are still a number of new processes and pieces of equipment design which are slowly becoming industrial standards.

This paper presents some selected developments and new products which should prove to be of common interest among paper makers of various grade ranges.

Pigment dispersion and coating colour mixing is known to have vital impact upon final coating mix properties. The pigment slurry is the largest single component of the coating colour formulation, and is also responsible for introducing the majority of the impurities. Inadequate processing can cause defects which are difficult to correct in subsequent process steps.

Ever increasing solids contents and viscosity levels of the coating mix demand a particular capability of the mixer in use. In fact there is a lot of equipment operating in paper mills today which simply offers inadequate shear and mixing properties.

As an alternative to installing a complete new mixer, however, there are available agitator retrofit packages which can improve mix preparation performance, without major capital investment.

Continuous coating colour preparation is becoming increasingly popular. It offers benefits especially in processes where few coating colour grades are required and particularly where formulations are quite similar to each other. The advantages which may be realised relate to investments costs, space demands, fast grade changes and minimised colour losses.

Batch processing, however, is still the most common technology in use today, and will likely remain so for the foreseeable future. There have been developments, mainly in dosing systems, recipe handling and automation. There are also novel dosing systems which make the usage of dry components a reality.

The majority of problems in the supply system are related to screening. There is a good choice of available technologies which better take into account the special features of each application, such as multistage screening, automated strainers, return line pressure screening, in addition to the development of a new screening element having round holes.

Centrifugal deaeration is today accepted as essential for use in conjunction with some coating technologies, but offers benefits, in fact to any method.

On line measurement of colour properties such as solid content, air content, rheology, pH and temperature is today commonplace. Coating methods have also been developed which allow complete elimination of return flow, which permits design of a very compact supply system, saving space and start up time and allowing much simplified clean up and servicing procedures.

Ultrafiltration is now one of the principal methods for coating effluent treatment, and is unique as a method which enables recycling of pigments and chemicals with retention of their full functional value. That is to say that the effluent concentrate can be used as a component of the new coating colour. In some applications, the limiting factor has been the concentrate solids at 25 - 35 % level. Adding a small second stage filter, however, can see this increase to 50% level, which allows higher dosing amount into the new coating.

## Today's trends in coating kitchens, supply systems and coating effluent treatment

The basic design of coating colour makedown systems has remained static for many years, due, in part at least, to a characteristic risk aversion on behalf of paper makers. The need for 100% reliability along with ingrained conservatism has prevented the introduction of too radical solutions into the market.

Even against this background, however, there are a number of new developments which are slowly becoming modern industrial standards.

This paper presents some selected improvements and new products offering common interest to a wide range of paper makers.

## Coating pigment dispersion and coating colour mixing

This area of technology is increasingly understood to have a vital influence upon final coating colour quality. Pigment is the principal component of the coating colour and is also responsible for being the source of the majority of impurities. Poor rheological characteristics of the pigment slurry is almost invariably related to inadequate first stage dispersion, and results in coating colour defects or deficiencies which are impossible to rectify in subsequent process steps. Non dispersed lumps or agglomerates, for instance, can cause severe problems such as coating streaks or blade scratches in the finished product.

Solids content and viscosity of the coating colour can be very high, making special demands on the coating mixer. In some formulations, dry components are specified to allow an increase in final mix solids level, to give enhancements in coater runnability and reduction in dryer load. Such applications are especially demanding due to the conflicting requirements of providing good mixing and high shear at the same time.

Almost all pigment dispersing processes are batch type processes, and this situation is likely to remain the case in future. Batch type mixers are occasionally used in continuous mode, but true in - line mixers are a rarity. The current perception of the problems encountered with in - line mixing are overall reliability, vulnerability and a general lack of controllability. Most installations are used as wetting devices only, and still require good post - mixing.

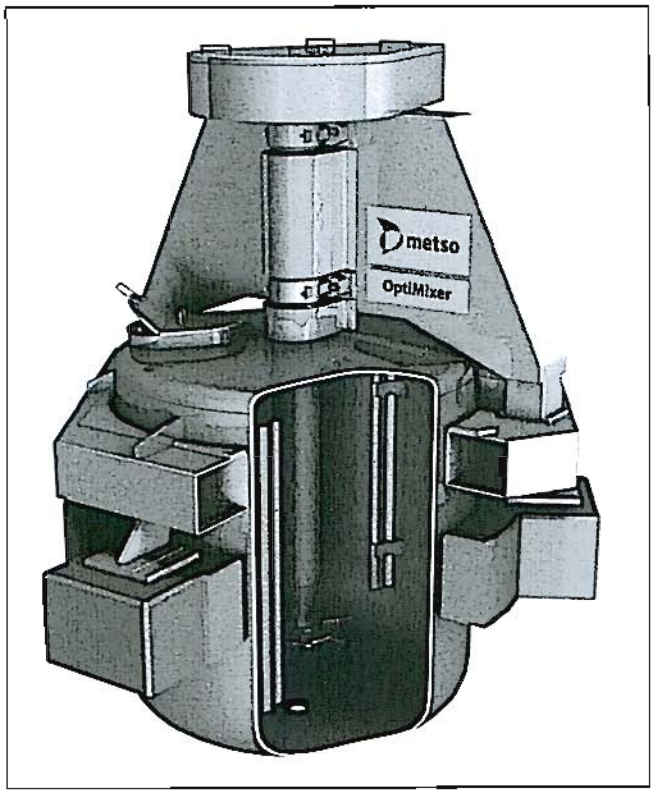

Figure 1: Top entry pigment/coating colour mixer

In coating colour preparation, however, in - line mixers are much more applicable.

Most of the pigment dispersion and coating colour mixers on the market today are quite old designs, with developments only in details or materials. These are categorised basically as bottom or top entry mixers: Referring to the geometry of the agitator itself.

Generally, bottom entry mixers suffer from necessarily having a relatively complex construction owing to the difficulty in sealing the shaft: They also tend to have limited ability to agitate the uppermost levels in a full mixer. In some rotor / stator constructions it is difficult to maintain good mass transfer, particularly with mixes of difficult rheology: The only solution found to ease the situation has been the use of adjustable stators.

The most successful all - round mixer designs have been proven to be of robust, top entry construction.

This geometry helps to guarantee good mass transfer and good dispersion in all circumstances. The simple, strong construction allows best runnability, easy installation of the mixer tub on load cells, and with no need for a complicated rotor seal.

*Figure 2* shows an advanced impeller design. Its design has been developed to allow both mixing and dispersing properties within a single unit. The device has a simple construction which allows fine tuning of the geometry on a case by case basis. This means that both pumping and shear characteristics can be optimised across a wide range of applications. Particular attention has been paid to material selection, and a highly wear resistant powder metal compound has been used.

There are many mixers operating within the paper coating business today which were built with inadequate shear or mixing capability, both in pigment makedown and in final coating colour preparation areas. It is possible to make a retrofit installation of the impeller design described above, which invariably

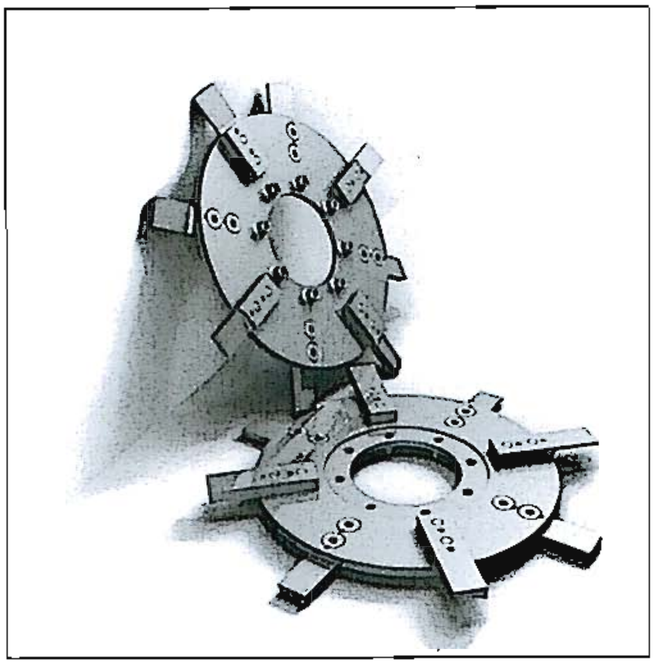

Figure 2: Special Barturbine impeller

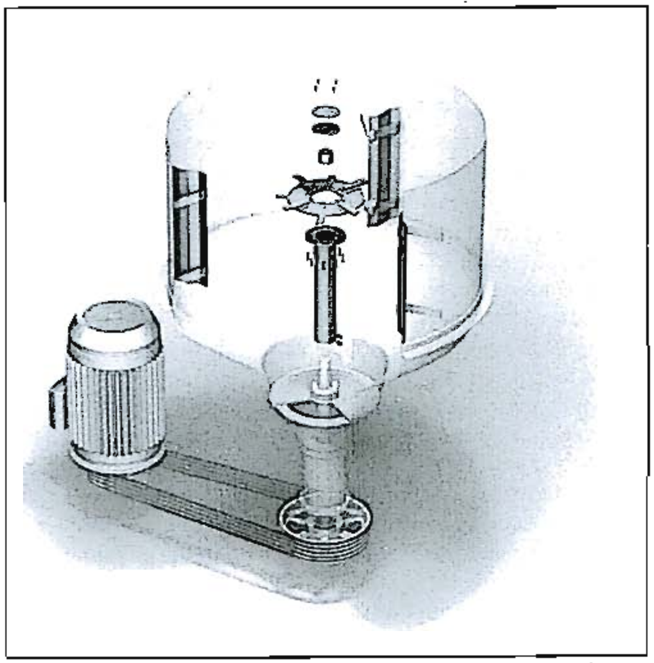

Figure 3: Mixer retrofit package to a bottom entry mixer.

proves to be a much more cost effective solution than a capital replacement of the mixer in its entirety. Following such a rebuild, the performance of the installation as a whole is, in every case, an improvement upon the original equipment, both in terms of mixer performance and in cost savings gained from maintenance enhancement.

## Coating colour preparation

### Batch coating preparation

The traditional batch coating colour preparation system is the absolute market leader, considering historical installations over several decades, and this situation is unlikely to change greatly in the foreseeable future. Despite the fact that the instal-

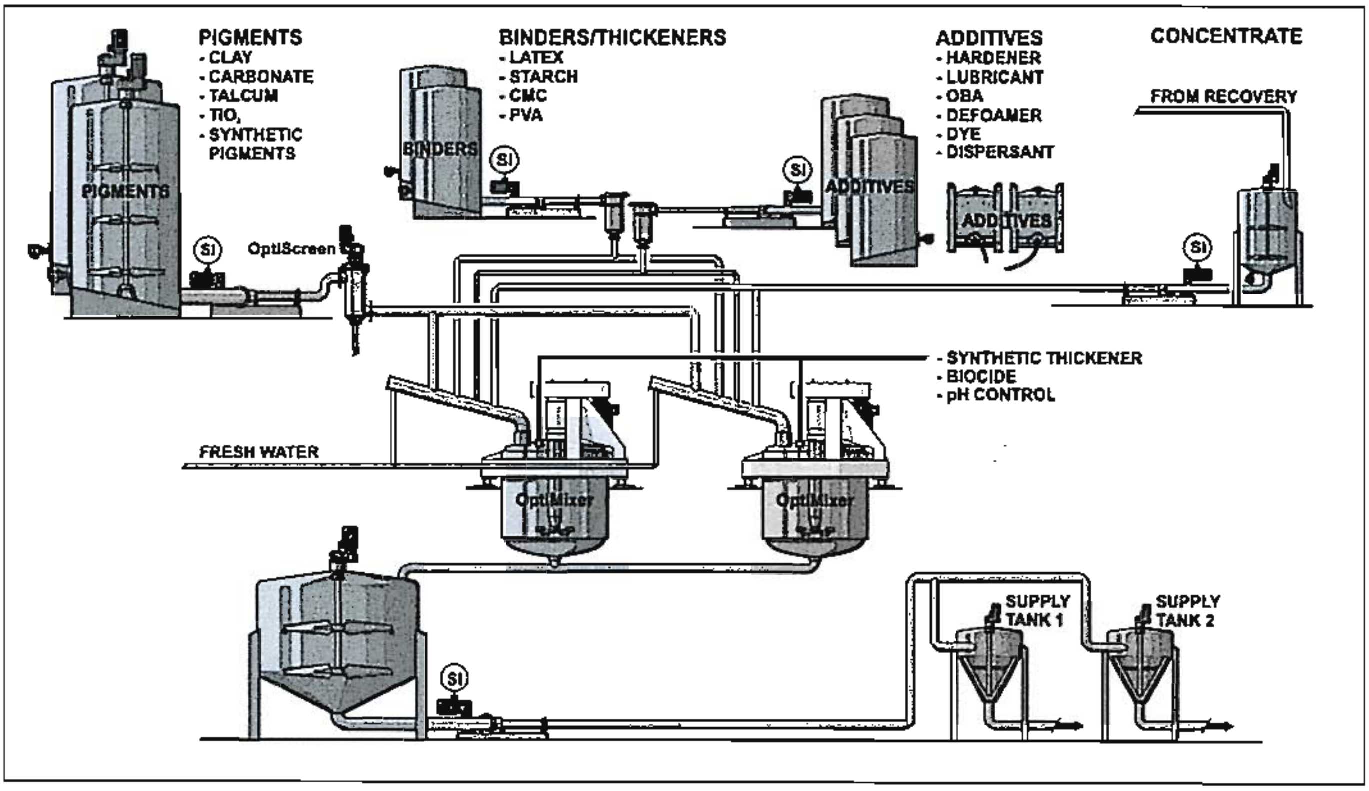

Figure 4: Principle batch coating colour process

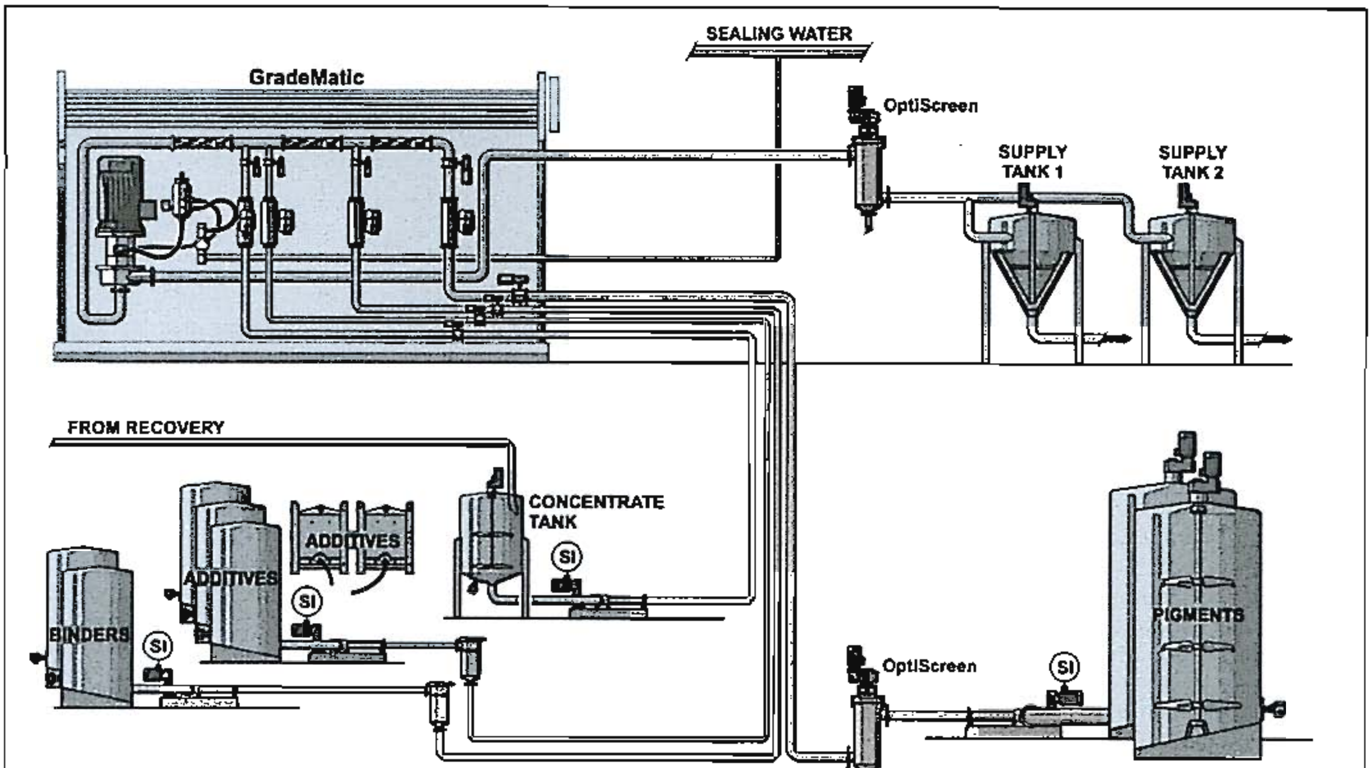

Figure 5: Principle of continuous coating kitchen

lations tend to be costly in terms of capital investment, as well as being space and maintenance intensive, they practically remain the only option for many paper makers. Main reason for this is probably based upon the legendary conservatism of paper makers, which in itself gives an endorsement of the absolute reliability of such traditional design.

No news from the coating kitchen? This is good news.

The batch process is flexible, insofar as it is capable of producing a wide range of colour formulations with varying recipes. Mainly, the areas which have been developed with batch technology are related to automation and instrumentation.

## Continuous coating colour preparation

Even if the advantages offered by the continuous system are, in some cases, obvious and even proven, there is still some resistance to acceptance of the technology, and the selection of either process is always based upon a very complex matrix of optimisation objectives.

This method of coating colour preparation is becoming more prevalent, but such change happens slowly.Experts in the field have been predicting the growth of continuous processes for many years now, but only recently has it started to appear that such a shift might actually be probable. Main reason for this is that the price, performance and reliability of the demanding automation and in - line flow control equipment which the continuous process requires has only recently become more applicable.

Basically, as of today, the coating colour quality and process runnability of both traditional and in - line processes are comparable.

In the in - line process, all components are metered continuously into the mixing unit. The flows of all components are measured and controlled by on - line mass flow meters and speed controlled pumps. Flow rates of the various components are adjusted according to the coating colour formulation, and the total overall flow is controlled by the consumption of the coating colour on machine. Directly from the mixer unit coating colour is transferred into the coater supply system and for most applications, no intermediate storage tanks are needed.

The order of mixing of components can be optimised, case by case: Following each dosing point, static mixing is utilised and the final dispersion of the whole is guaranteed in a mechanical in - line mixer. Since all of the equipment within the system is comparatively small, it is possible to house a complete, functioning installation within a compact rig. *Figure 6* shows such a continuous "plug - and - play" coating kitchen. It houses all of the necessary devices and instrumentation to guarantee accurate dosing and complete mixing with the special integrated in - line mixer.

The system offers clear benefits for applications where few and similar coating colour formulations are required. It is particularly applicable also where short installation times are demanded, as well as installations where available space is at a premium. Savings can also be made, owing to reduced effluent losses, owing to the small volumes involved, and the highly

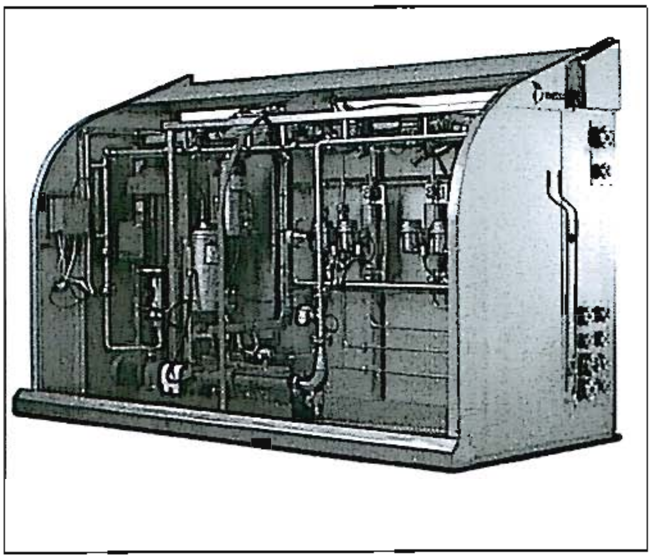

Figure 6: Continuous kitchen rig

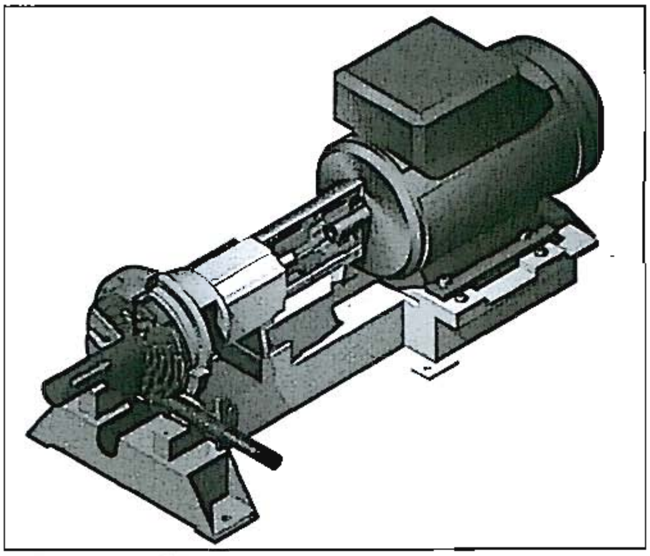

Figure 7: In-line coating mixer

| Batch | Continuous |
|---|---|
| • "Traditional, reliable"<br>• Suitable for multi grade and several stage coaters, very flexible<br>• Batch time 35 - 60 min<br>• Need for coating storage tanks<br>• Larger overall space demand<br>• Sharp grade change possible<br>• Easier to disperse dry components<br>• More difficult to handle effluent amount because of large volumes<br>• Total investment cost ? | • "New, unknown"<br>• Suitable for single grade machines with small formulation variations<br>• Short retention time, only minutes<br>• No need for coating storage tanks<br>• Smaller overall space demand<br>• Grade change even sharper<br>• Dispersing dry components difficult<br>• Small effluent amount because of small volume<br>• Total investment cost ? |

Table 1: Comparison of continuous and batch coating colour preparation

efficient grade changes which are facilitated by the system. Any coating methods requiring air - free coating colours are also accommodated by this closed system, since the system can operate under slightly elevated pressure.

Doubts regarding system reliability are simply no longer valid, as the modern technology utilised within these installations guarantees reliable and trouble free operation to rival that of a traditional batch preparation system. *Table 1 (previous page)* sets out the pros and cons of each competitive system. It can be seen that the final choice depends upon numerous parameters such as investment costs, space availability, number and type of coating colour formulations, grade change frequency and effluent losses.

## Mixing of dry components into coating colour.

It is a very common target to increase coating colour solids to give advantages in finished product quality, as well as savings in coating drying. It is a fact in many applications that no additional water will be added in the coating kitchen. One of the major water sources which can possibly be eliminated is that added as part of the thickening component: For example, CMC is normally dosed as a 10% solution. If 0.5 parts of CMC is added, this results in a coating colour solids reduction of 2%.

Adding CMC in the dry state, however, is not straightforward. It is all to easy to form large sticky lumps with dry CMC at their centres. Complete dissolution of these lumps can take tens of minutes, and so manufacturing capacity is impacted.

Recent development of a new premixing system, however, makes it possible to add dry powder components such as CMC in a batch makedown system without the need to increase cycle time. In this system, the dry powder is premixed, in a special chamber, with incoming pigment slurry, during its introduction into the main mixer. The dry component is so evenly distributed in the premixer, and into such small particles, that dissolution takes place very rapidly. This makes it possible to increase final coating mix solids significantly without loss of kitchen capacity.

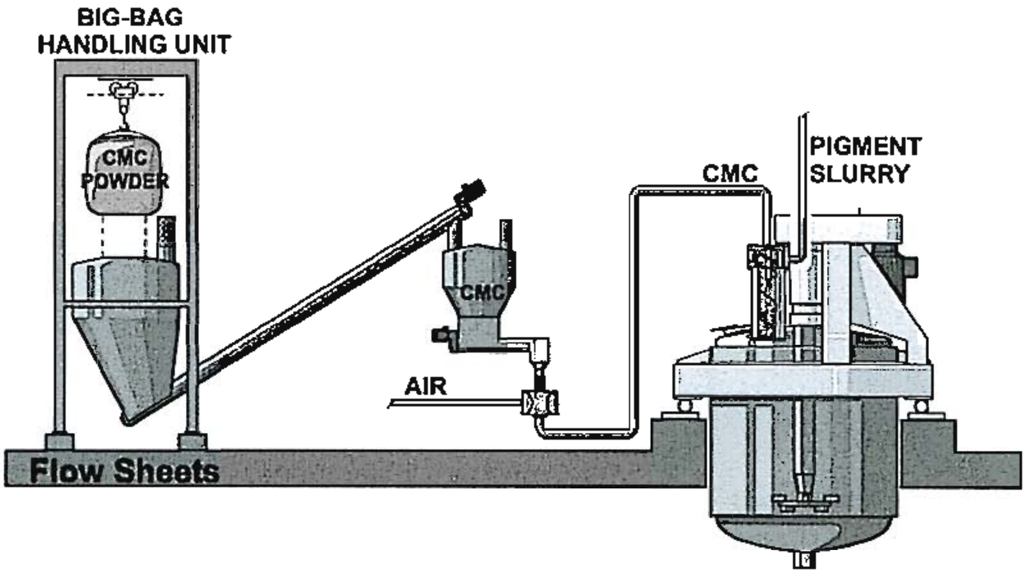

Figure 8: Dry component pre-mixing system

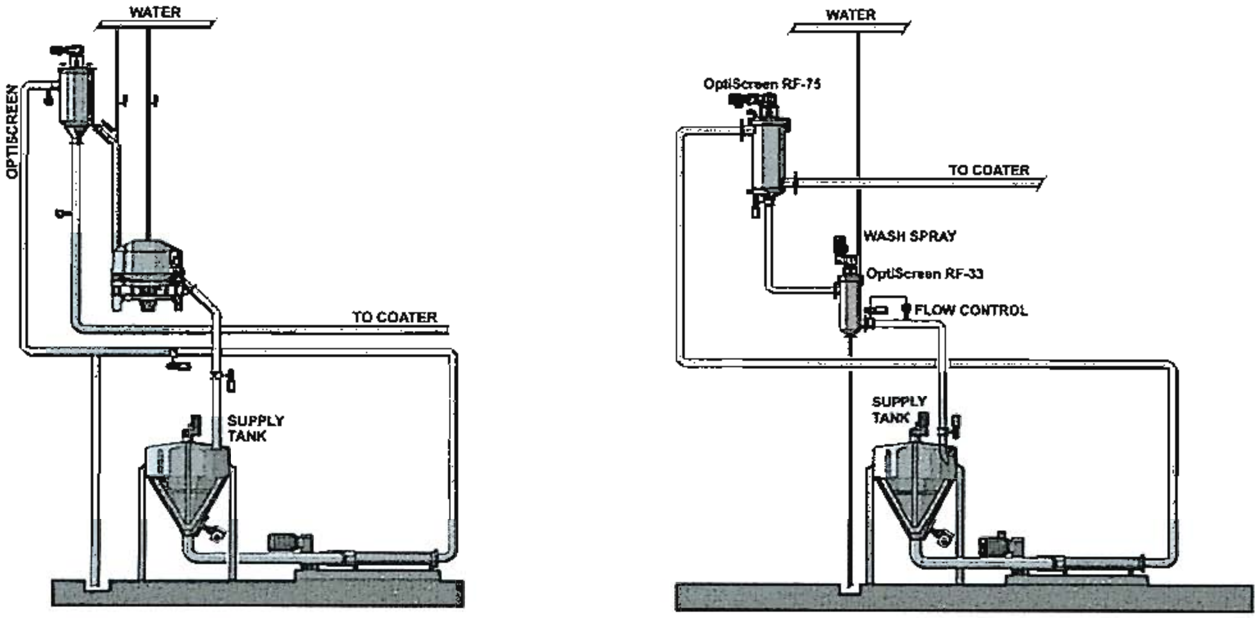

Figure 9: Double screening with vibrating screen or pressure screen as secondary screen

## Supply systems

### Screening concepts

Coating colour screening historically was performed with so called backwash screens. These had many drawbacks, including complex construction, hence high maintenance requirement, high effluent losses, plus the ever present risk of coating colour dilution. These have been largely superseded today by mechanically doctored pressure screens fitted with slotted wedge wire baskets as the screen element. Today, there is invariably at least a single stage mechanical pressure screen between the machine tank and coating head.

Quality demands are ever increasing, and the range of coating colour formulations is becoming even more complex. There is a clear need to adapt screening concepts to consider paper grade, mix formulation, coating method and base paper characteristics: For instance, it is reasonable that we would propose a different screening process solution for a testliner size press installation than for a fine paper top coating duty. It is important not just to utilise ever finer screening, but to understand fully the application, and develop an optimised solution.

There are a number of new screening concepts now available which give clear benefits when compared to traditional single stage screening.

## Double screening

If there are many and various impurities to be sorted by the screening system, where handling in a single stage may be difficult, it can be advantageous to arrange screens into multiple stages.

The primary screen can continuously reject to the secondary screen, which can be either a pressure screen or a vibrating screen, depending upon the application. This makes it possible to purge and flush the secondary screen without disturbing the

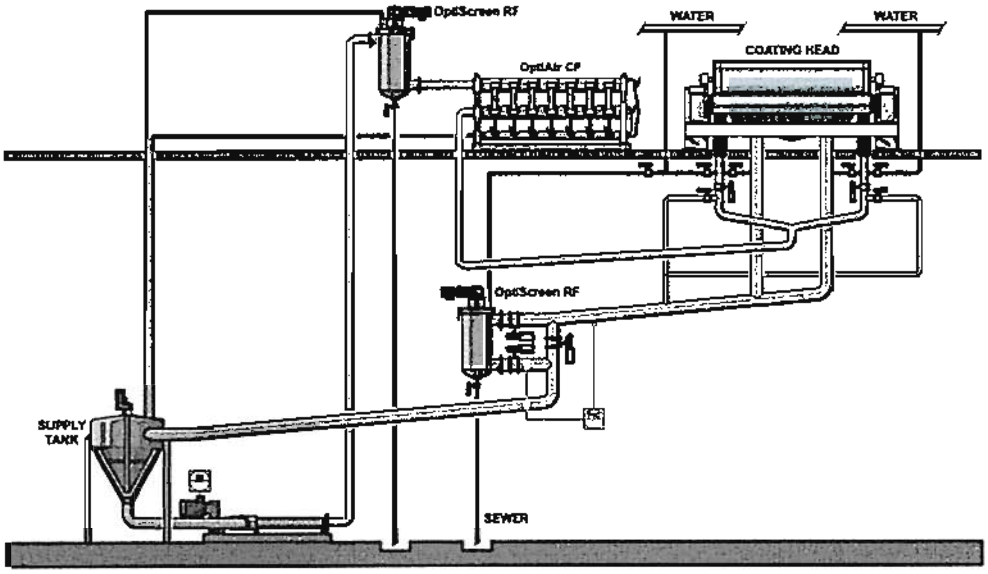

Figure 10: Return flow pressure screening

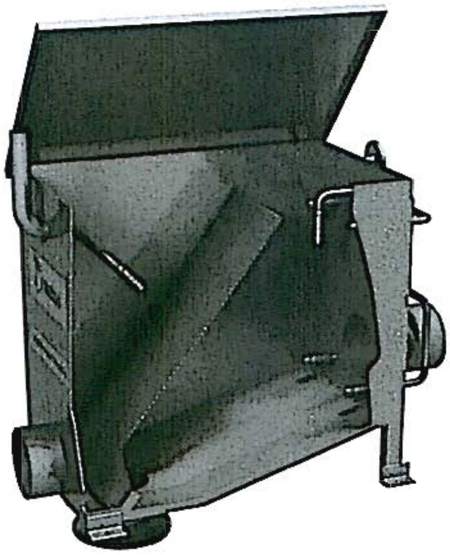

Figure 11: Automated return flow strainer

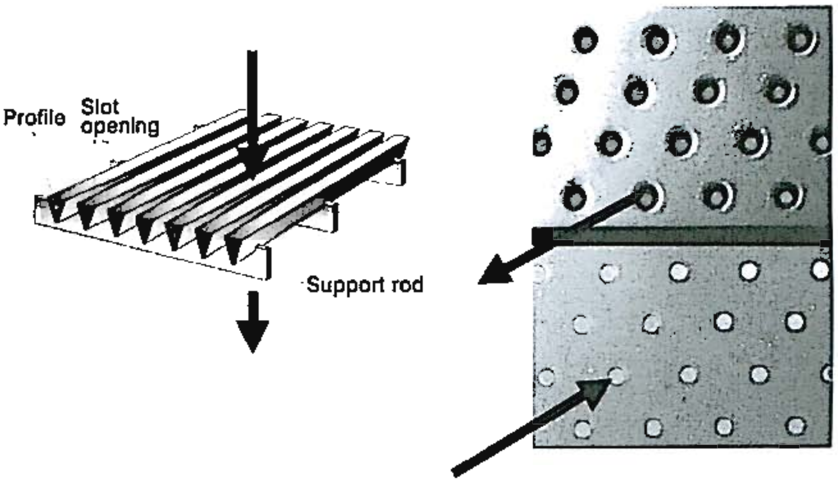

Figure 12: Wedge wire and round hole screen elements.

main process. The secondary screen is typically finer than the primary, thus increasing separation efficiency. Effluent amounts are reduced, and the maintenance needs of the primary screen is decreased.

## Return flow screening

It is possible to add pressure screening in the return flow line without additional pumping capacity, if there is adequate height differential. That is to say that static head is used to generate differential pressure. Purging and backwashing can be performed without affecting the process, and impurities are removed immediately as they enter the circulation system. The use of static head differential ensures that the screen drum can never be damaged by over pressurisation.

## Automated strainers

The first fully automated coarse screens have only recently entered the market. The new strainer prevents paper pieces and other debris from entering the supply system during web breaks, and automatically removes them to sewer.

## Screen element materials

The majority of screen baskets for pressure screens are made from wedge wire. Wire is wrapped into a basket form, and the space between subsequent wire layers forms the desired continuous slot. This design of basket is likely to remain the standard choice, even though it offers intrinsically imperfect separation efficiency, owing to the two dimensional

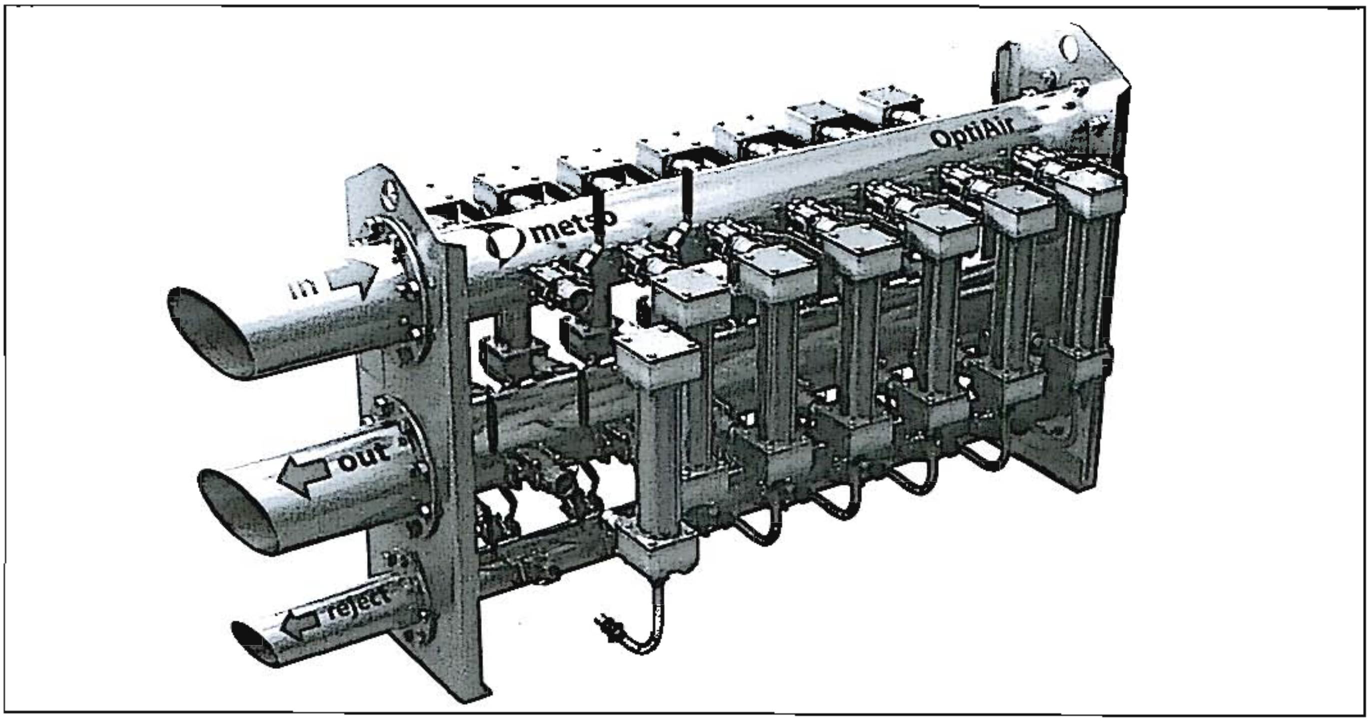

Figure 13: Cyclone deaerator

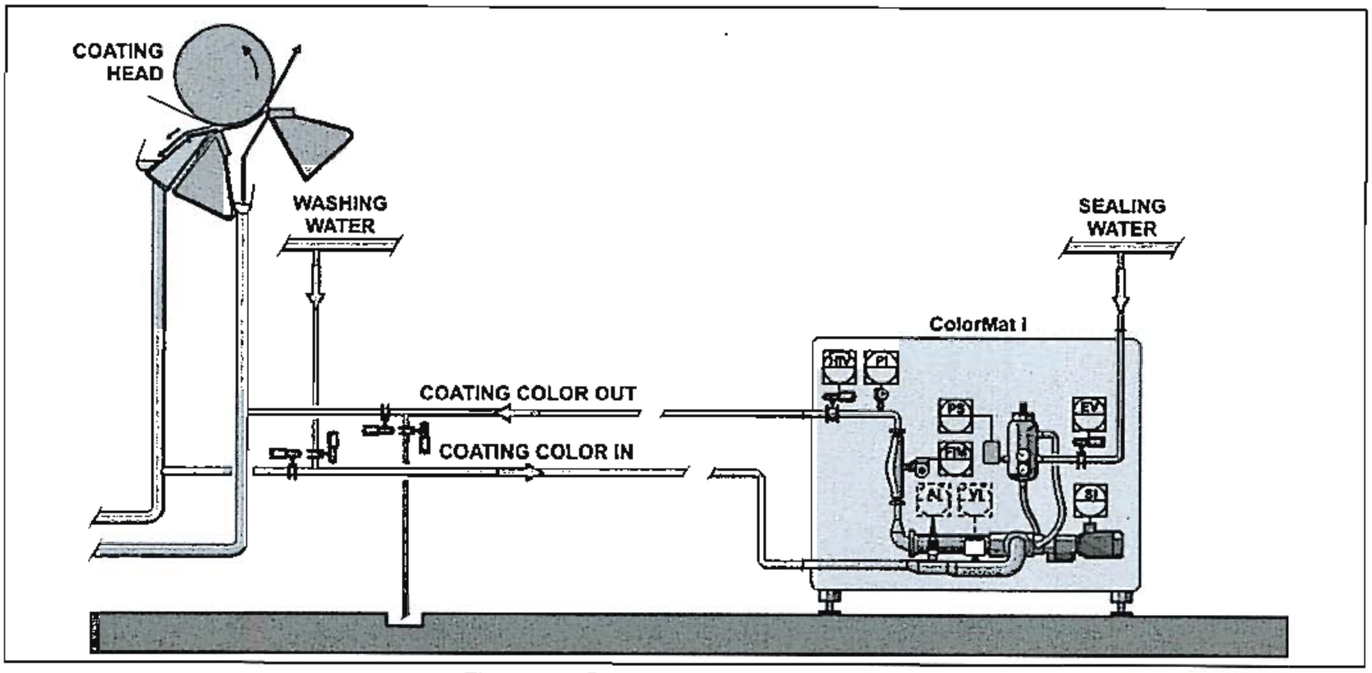

Figure 14: On-line measurement system

slot. It does, of course, offer good structural strength and very high capacity.

Only recently available are screen baskets with round holes or circular perforations of sufficient fineness to allow good separation efficiency. Even though their capacity is not great, they offer good performance in specialist applications such as fresh colour screening, double screening applications, and fibre and felt hair removal.

Other material choices such as wire mesh or sintered plates offer only marginal utility in coating colour screening applications.

## Deaeration

Centrifugal or cyclone deaeration is absolutely required in certain applications such as free jet coating, since skip coating is otherwise observed, relating to the presence of air bubbles.

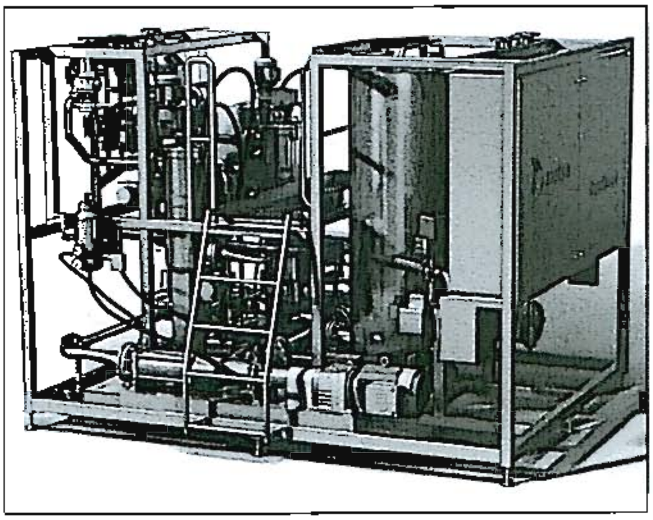

Figure 15: Compact supply system design

Deaeration is gaining popularity even in other coating methods, however, not because of any noticeable quality improvement, but because it reduces the reliance upon, for instance, anti foam chemicals, and normally tends to stabilise the process significantly, giving assured operability.

*Figure 13 (previous page)* shows a typical deaerator offering consistent, reliable function, simple construction and easy operation and maintenance.

## On - line measurement of coating colour properties

The on - line measurement of the major coating colour properties - solids level, air content, rheology, pH and temperature - is, today, a reality.

Frequent, precise measurements can be used for process analyses, and to forecast potential process disturbances. There are currently no systems which allow actual control of these parameters, although these are in development. It is probable that the first parameter which will be controllable under closed loop will be solids content. The system shown in *Figure14* takes a small continuous flow from the supply system, through the analyser, and back into the process stream. Measurement of air content and solids level is based upon measured density at different pressure levels. Rheology is measured by capillary viscometry across different shear ranges. Temperature and pH measurements are of course options. It is envisaged that these analysers will become ever more integrated as the regular part of a coating supply system, along with interfacing with the mill automation system.

## Compact supply systems for closed chamber sizers

Coating methods which employ zero return flow raise the possibility of packaging the entire supply system into a single, compact rig. This concept offers remarkable savings in space demand and installation and startup times.

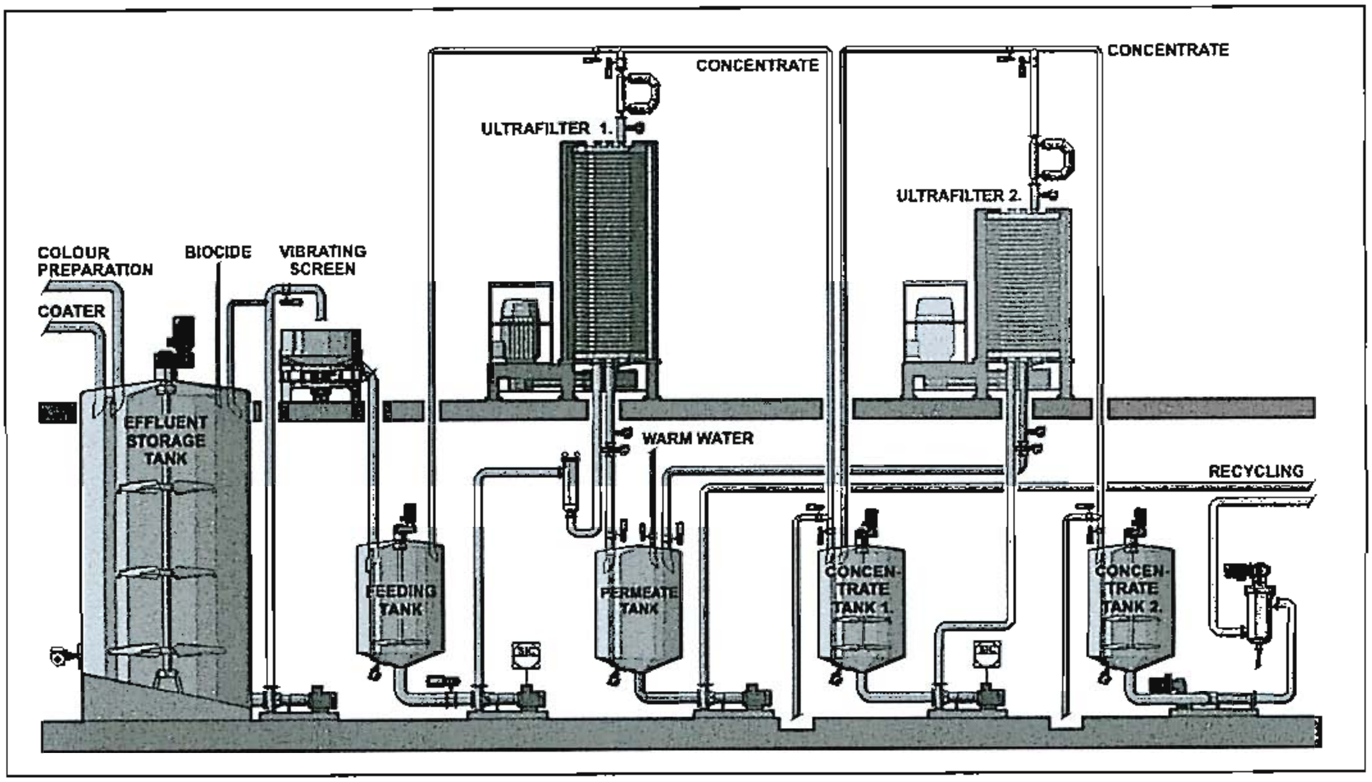

Figure 16: Ultrafiltration process with additional second stage

## Coating and effluent recycling

Broadly speaking, there are today two main methods for recovering coating effluent materials. Some mills mix coating effluent with the coarse centricleaner fraction, fine grind the mix and use it as part filler supply. This is of course functional, but suffers from certain devaluation of the recovered fraction, since coating pigments are invariably more expensive than filler pigments. Binders and other coating chemicals are additionally either worthless, or even harmful to the paper making process.

Ultrafiltration is a process whereby not only the coating pigments, but also the coating binders and other components can be recovered and reused, at full value, in fresh coating colour formulations.

In the Ultrafiltration process, hermetically salvaged effluent, typically in the range of 1 - 3 % solids is pumped to a filter unit comprising semi permeable membranes with mechanical agitation.

The pore size of the membranes is such that water and other smaller molecules are able to penetrate, while suspended solids and more complex dissolved or colloidal molecules cannot.

Most coating effluent filters utilise polymer membranes. The effluent stream feeds into one end of the unit, water is continuously extracted, and solids content is increased towards the discharge end. Mechanical agitation generates turbulence at the membrane surface, and ensures that no "filter cake" is formed. The final out flow stream solids is controlled by the retention time within the filter unit.

Since the concentrate consists of only the original coating colour components, and no filtration additives such as coagulants or flocculants are used, the material can be reused directly in fresh coating colour with no quality concerns.

*Figure 16* shows a flow sheet for an Ultrafiltration system utilising polymer membrane separation medium.

There are also ceramic ultrafiltration processes available in the marketplace: These are of tubular construction, and turbulence is generated by high flow velocities. They have limited use in paper coating applications, as they tend to clog as solids levels and viscosities increase.

In some applications, the limiting operating factor also with polymer membranes has been the maximum achievable concentrate solids, at 25 - 35 %. In traditional single stage filtration, it is not possible to further increase solids level safely and practically. The addition of a small secondary filter however, can eliminate this deficiency, raising the process solids content to 50%: This then satisfies all practical needs to allow subsequent material utility.

This optional layout is also shown in *Figure 16*.

# NOTES

# Round Table Discussion

*Moderator*
**Ian Davis**

## NOTES

# NOTES

# Design and Engineering of Mineral Fillers for Barrier Coatings

*by*
**Dave Gittins, Hannah Howard**
**and Bob J Pruett**
Imerys Minerals

SESSION FOUR
PAPER SIXTEEN

**Due to the late inclusion of this paper within the conference programme it has not been possible to include this paper prior to print**

# NOTES

# New Developments in Print Receptive and Barrier Coatings

*by*
**Robin Cooper**
New Business Development Manager
Michelman Int'l & Co

SESSION FOUR
PAPER SEVENTEEN

## Summary

This paper describes two recent developments
- A size press treatment for uncoated papers that will improve ink adhesion to the substrate.
- Moisture vapour and grease resistant barrier coatings both on-line and off-line at the blade coater.

## Print Receptive Coating

Digital printing techniques are becoming increasingly important for both commercial printing and industrial packaging. One of the techniques that is at the forefront of this growth market is the HP Indigo printing press. This press is unique in that it uses a liquid toner [US Pat Nos 5,225,306;5,276,492;5,346,796 and 5,407,771] for use in an electrostatic printing technique. This liquid electrophotographic ink is better known under the trade name ElectroInk. The limitation of these types of inks compared to more conventional inks is the adhesion of the ink to the substrate. The ElectroInk will generally adhere properly to the substrates only with additional help or 'optimisation' of the substrate.

The 'optimisation' process is basically preparing the surface to accept and adhere to the ink. The ink is transferred to the paper under the action of temperature and pressure. See *figure 1*.

To describe the process simply:
1. Electrostatic charging of the electrophotographic Photo Imaging Plate (PIP) which is mounted on the imaging cylinder.
2. Exposure of the PIP to laser light. The lasers are given binary off/on instructions from the digital computer file.
3. Image development performed by the Binary Ink Developer units (BID).
4. Transfer of the inked image to the blanket cylinder.
5. Any residual ink and electrical charge is removed from the PIP.
6. Heating of the inked image carried by the blanket.
7. Transfer of the heated inked image to the substrate held by the impression cylinder.

The adhesion of the ink to the substrate must be such that the image formed on the heated blanket is fully removed and transferred to the substrate.

To best enable this transfer the surface of the paper needs to have the following properties:
- Good chemical bonding to the ink binder, the image must prefer bonding to the substrate rather than remaining on the blanket
- A high green strength of this bond to completely remove the inked image from the blanket
- The surface chemistry should not affect the ageing properties of the Image.

The approach we have taken is to use a thermoplastic polymer that is chemically compatible with the ink binder and possesses high hot tack so that the image is stripped from the blanket under the influence of heat and pressure. This in itself

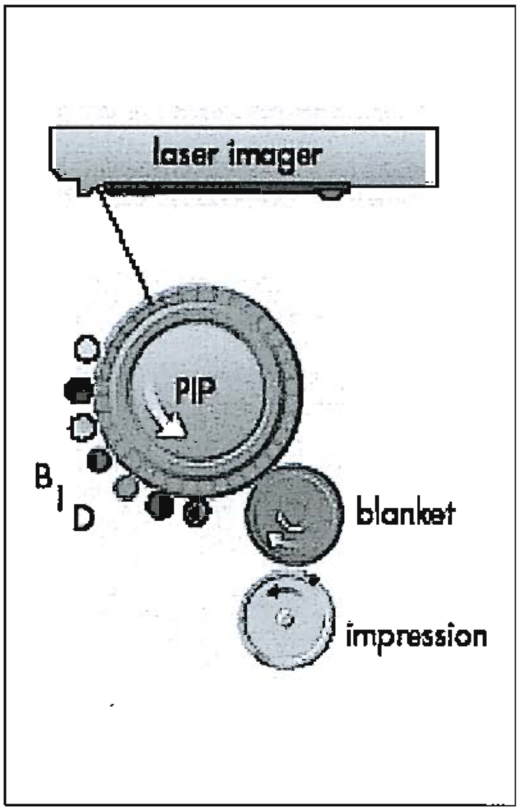

Figure 1

is a challenge but the more testing challenge is to make these products applicable by conventional size press techniques where the heat activation of the surface could be a major concern in production - the paper typically is contacting drying cylinders for instance. To overcome this potential problem it is necessary to incorporate a thermosetting component into the formulation and to balance the ratio of the thermoset to the thermoplastic.

Happily the thermosetting material we decided to use was one that is well known to most paper makers - starch. We also realised that because of geographical and local production requirements we would need to find classes of starch that would be compatible with the thermoplastic polymer so as to give the paper maker the widest choice of suppliers.

We carried out stability tests using various starches by measuring the viscosity of the mixtures held at 55°C for 24 hours. To pass the test the solutions had to remain below 75 cP.

We found that the chemically modified starches gave considerable stability advantages over native starches when mixed with the thermoplastic polymer and that with these types of starch we had improved latitude for the incorporation of the thermoplastic polymer. Based on print tests we found that the ideal starting ratio of the starch to thermoplastic polymer was 1:1 on a dry solids basis.

To enable better compatibility the thermoplastic polymer is emulsified in water at a near neutral pH, it has a 35% solids content with an average particle size of 120nm and is a low viscosity milky dispersion. The product is called DigiPrime® 1500LA.E.

The following performance criteria of the coated sheet are assessed:

**Runnability-** The ability of the size press coated paper to run smoothly through the press without blocking or other mechanical feeding problems.

**Ink transferability-** The quality of ink transfer from blanket to substrate-no ink should remain on the blanket.

**Blanket-Substrate Compatibility-** The so-called 'stress mode' where long runs with controlled images are made on the press and any reduction of image quality is noted.

**Ink-Substrate Interaction-** The degree of ink to substrate adhesion. This is assessed using a standard 3M 230 adhesive tape which is carried out immediately, 15 minutes, 1 hour and 24 hours after printing.

DigiPrime® 1500LA.E is currently being used by several paper makers globally to provide paper that will receive digital images.

## Barrier Coatings

The use of barrier coatings on paper and board packaging has given substantial benefits to producers, retailers and consumers. Barrier coatings improve product protection either from the environment or to protect the environment from the product. This can result in increased shelf life, reduced wastage, increased convenience, improved presentation and enhanced product safety.

With the variety of materials available to packaging producers, the choice of barrier materials is a highly competitive market and the paper and board industry is constantly changing to keep pace with strong threats from other packaging materials.

Environmental concerns are clearly influencing current decisions concerning barrier technology. Concerns about recyclability, energy conservation and air pollution are leading to a reassessment of available barrier technologies. Paper- based barrier materials are perceived very favourably due not only to their recyclable properties and infrastructure but also their renewable raw materials.

Barrier coated paper and board consists of several different types of material. For purely grease and oil resistant paper and board, the surface application of flourochemicals as barrier coatings were developed as size press applications. Another halogenated polymer system that can be applied to paper and board and offers gas barrier properties is PVdC. Doubts have been expressed about halogenated coatings because they can produce potentially harmful degradation products.

For barriers to water and water vapour, traditionally the choice has been to use off-machine lamination or extrusion technology where a film of polyolefin (PE,PP or PET) is combined with the paper and board substrate. This requires specialised equipment but a coherent film is produced that, as well as giving a barrier to liquids, can provide good performance as a moisture vapour and aroma barrier. Laminated or extrusion coated paper and board can be difficult to re-pulp and are seen as a composite structure.

Paper and board has been treated with waxes for many years to give water hold out and resistance to water vapour. The main criticism of these products is that when used in large amounts in the recycling process they can cause problems with 'stickies' and hinder recycling. They often have a negative impact on the coefficient of friction of the recycled paper as well as interfering with fibre to fibre bonding.

There has been interest towards using water based emulsion technology since they offer a recyclable product with good barrier properties to water, oil and moisture vapour. These coatings when applied to paper and board can also be classified as a monomaterial and not as a composite structure. Being water based these coatings can be applied using conventional paper coating techniques although the application technology can have a major influence on the barrier properties achieved.

| Coating Material (Dry weights) | Temperate MVTR (gsm/day) | Tropical MVTR (gsm/day) |
|---|---|---|
| 25 gsm LDPE | 5 | 20 |
| 25 gsm Wax | 3 | 15 |
| 8 gsm PVdC | <2 | <10 |
| 5 gsm VC2200 | <5 | <20 |

Table 2. Moisture Vapour Transmission Rates (MVTR)for typical coatings

| Starch Type | Max % Solids | Max % Thermoplastic polymer | Viscosity Stability at 55°C |
|---|---|---|---|
| Hydroxylethyl modified corn starch | 10 | 75 | Good |
| Ethylated corn starch | 10 | 75 | Good |
| Acetylated corn starch | 8 | 25 | Good |
| Ethylated potato starch | 8 | 75 | Good |

Table 1.

In work previously published [S G Yeates, M Passier, R Satgura, J Farre Europ Coat J p294 (5) 1995] it was shown that although low Cobb values could be achieved by using hydrophobic styrene acrylic polymers, the use of wax was seen as essential to obtain good MVTR performance. The disadvantages of using wax in emulsion polymer barrier coatings have also been discussed by other authors [K Santamäki, 'Highly filled dispersions as barriers', 1st International Polymer Coating Conference: June 9-10 1997, Tampere University of Technology]. These were said to be:

- Low surface energy leading to difficulty in glue and print acceptance on the barrier coated surface, i.e. surface energy <35 dynes/cm
- Low paper to paper friction, causing handling problems on automated systems.
- Repulpability, wax present in repulped paper can cause reduction in inter-fibre bonding capacity and hence paper strength.

Santamäki suggested using pigmentation as a way to achieve barriers to water, moisture vapour and oxygen transmission.

To achieve barriers to gas transmission, it is important to understand how the gases permeate through a film. Permeation is a three-part process and involves solution of small molecules in the polymer, diffusion through the polymer according to the concentration gradient, and emergence of the small molecules at the outer surface. Hence permeability is the product of solubility and diffusion and it is possible to say:

$$P = DS$$

Where P is the permeability
D is the diffusion coefficient and
S is the solubility coefficient.

Some authors (XX V Stannett, M Szwarc, J Polym Sci 16, 89 (1995)) have argues that the permeability is a product of a factor F determined by the nature of a polymer, a factor G determined by the nature of a gas and an interaction factor H (considered to be of little significance and assumed to be unity). Thus the permeability of polymer 'a' to gas 'b' can be expressed as

$$P_{ab} = F_aG_b$$

From a knowledge of various values of P, it is possible to calculate F values for specific polymers and G values for specific gases. If the G value for one of the gases, usually Nitrogen, is taken as unity, the following values are obtained.

Crystalline structures have a much greater degree of molecular packing and the individual lamellae can be considered as almost impermeable so that diffusion can occur only in amorphous zones or through zones of imperfection. Hence, crystalline polymers will tend to resist diffusion more than either rubbery or glassy polymers. Apart from halogenated polymers, there are few crystalline polymers in water based form exhibiting the low toxicity and water resistance required to be formulated into a barrier coating. Hence the use of pigmentation is seen as an alternative way of introducing crystallinity. However the polymer binder is still potentially the weakness in this type of system together with the polymer-pigment interface.

In *Figure 2 (overleaf)* three formulations are compared formulation 1, formulation 2 and formulation 3. The MVTR results are plotted for two conditions - tropical (90%RH, 38°C) and temperate (50%RH, 23°C). Formulation 1 is a product relying on mineral filler to provide barrier with a binder based on a polymer which is essentially crystalline but with some amorphous regions. Formulation 2 is a product based on the same mineral filler but with a binder based on a rubbery polymer and formulation 3 is a product that utilises a waxy component to provide the MVTR barrier.

It can be seen that formulation 3 gives the lower MVTR under all conditions and at a much lower coating weight than the filled products. This can be explained by considering that the waxy component exists as a crystalline layer at the coating surface. Only a relative thin coating thickness is required to achieve an effective barrier. By contrast the mineral filler requires a tortuous path to be made as the 'weakest link' the polymer binder is evenly dispersed throughout the product. Here there is a necessity to have a certain thickness of coating to achieve a given barrier. However, we can see by comparing formulation 1 and formulation 2 that contain the same mineral filler that the polymer choice has a major effect on barrier properties. Surprisingly given the data in *Table 2* we find that the results in *Figure 2* a rubbery polymer binder gives a better performance than a partially crystalline polymer binder.

This suggests that there are other phenomena operating to affect the barrier to moisture vapour. Probably one of these is the adhesion of the binder to the mineral. We could imagine that in formulation 1 we may have poor wetting between the mineral and the polymer giving rise to 'flaws' within the coating. These may not exist in formulation 2. Similarly all of the binders are emulsion polymers and contain surfactants and/or

| Polymer | F | Nature of polymer |
|---|---|---|
| PVdC | 0.0094 | Crystalline |
| PET | 0.05 | Crystalline |
| Plasticisied cellulose acetate | 5.0 | Glassy |
| Low density polyethylene | 19.0 | Some Crystalline |
| Polybutadiene | 64.5 | Rubbery |
| Natural rubber | 80.8 | Rubbery |

| Gas | G |
|---|---|
| $N_2$ | 1.0 |
| $O_2$ | 3.8 |
| $H_2S$ | 21.9 |
| $CO_2$ | 24.2 |

Table 3.

surface active ingredients within their formulations. It is easy to imagine that these ingredients could aid transport of water vapour through a polymer, essentially increasing their F value.

In practice to achieve MVTR barriers on rod or blade coaters we have two main choices. Either a low surface energy coating containing a waxy component which will not be gluable or printable with water based glues or inks or a high surface energy coating utilising a mineral filler that will be gluable and printable but will require a higher coating weight to achieve a low MVTR. In *Table 4* a brief summary of two of our current commercially available products and their properties is given.

The further development of water-based barrier coatings is an ongoing process and currently we are looking at novel polymers and methods to disperse them in order to offer an improved window of performance for coated paper and board.

| Dry Film Property | VC2200 | VC892 |
|---|---|---|
| Surface Energy (dynes/cm) | <35 | >50 |
| Transparent | Yes | No |
| Glossy | Yes | No |
| Target dry coat weight to achieve Tropical MVTR <20 gsm/day | 8 gsm | 25 gsm |
| % Solids | 40 | 62 |
| Therefore recommended wet coat weight | 20 micron | 40 micron |

Table 4.

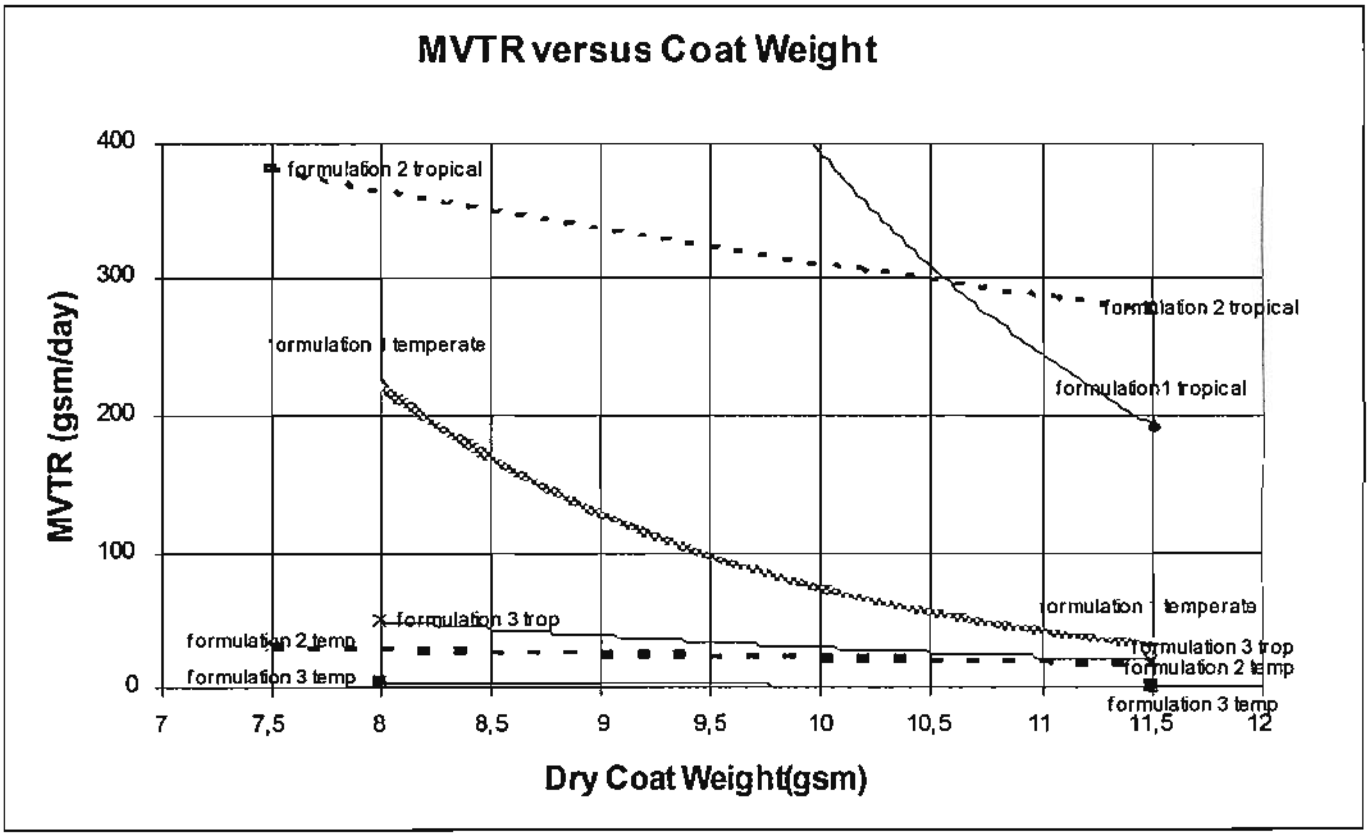

Figure 2. MVTR (gsm/day) versus Dry Coat Weight (gsm)

# Print, Packaging and Product Uniformity Issues through the Production Cycle

*by*
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SESSION FOUR

PAPER EIGHTEEN

## Introduction

Paper-based packaging combines two attributes:

- Providing a medium for the display of advertising, brand and consumer information
- Protection for the pack contents.

There is a necessary compromise between provision of an ideal base for coating, print performance and image quality and an ideal protective structure for pack contents. This compromise is not found in graphic printing grades to the same extent. Other performance aspects are dictated by the converting process, eg:

- Frictional properties
- Wettability and absorbency for gluing and functional coating
- Z-directional viscoelasticity for die cutting, creasing and folding
- Dimensional stability

These criteria must be balanced against the maintenance of coating properties - brightness, whiteness, opacity, ink receptivity etc.

Current market trends tend to emphasise the need for uniformity, namely:

- Downgauging - reduction of packaging mass
- Increased speed of converting and pack filling lines
- Innovations in pack design
- Barrier and heat-sealing functionalities
- Digital print
- Traceability and anti-counterfeiting
- Point of sale display
- Smart packaging - eg condition monitoring.

## Product categories and characteristics

Coated packaging production originally centred on traditional grades such as:

- Solid bleached - SBB/SBS (woodfree)
- Liquid packaging board - (woodfree)
- Solid unbleached - SUB/SUS (Kraft)
- Folding boxboard - FBB/GC1/GC2 (mechanical - TMP)
- White lined chip - WLC/GT (recycled)

In recent years, the unbleached categories have extended to include drinks wraps (six-pack) as well as frozen food packaging, formerly the preserve of bleached grades.

The development of point of sale and shelf-ready packaging has stimulated the use of coated liners for standard profile corrugated, where print quality is essential for customer appeal. The print may be applied by either pre-print (eg litho-laminate) and post-print methods. The use of pre-coated outer liners in corrugated has extended to microflute - E, F, N profiles. Microflute has taken coating technology into new areas and substrates, notably liners below 100 gsm. In this grammage range, there are opportunities for producers of coated printing grades in the development of lightweight fully bleached liners, eg for food and pharmaceutical packaging.

Coated label stock is a segment that spans packaging promotional and communication categories. Narrow web printing has seen the advent of digital print capable of producing up to 40,000 labels per hour. Self-adhesive labels without a release layer have also been evolved, a reminder that functional coatings, ie pressure sensitive adhesives and release coatings are a significant element in packaging. For some applications, the label or banderol contributes significantly to the strength of the pack. In thin-walled plastic yoghurt cartons, the label forms a continuous restraining band around the garden and contributes to its rigidity. This function requires good tensile strength in relation to grammage.

## Barrier and functional coatings

Barrier coatings can either keep materials within the pack, eg oil, grease, moisture, aroma etc, or keep them out, eg moisture away from dry goods and washing powder and odours and taint from sensitive products. Traditionally, barriers used either extruded polymer laminates, eg the polyolefin coatings applied to liquid packaging board, or the fluorochemicals, non-film forming compositions that rely on low surface energy to resist wetting eg for oil and grease resistance in fast food packaging.

The advent of water based barrier coatings (WBBCs) has enabled the development of products with an intermediate range of properties between the absolute barrier of polyolefin film and the more ephemeral barriers afforded by fluorochemicals. WBBCs also offer the possibility of selective barrier properties, eg, in the packaging of bakery goods where 'breathability' is needed, and of heat-sealing properties necessary for liquid packaging and cup stock. The success of the water-based coating will depend on the level of uniformity permitted by the base sheet. One pinhole can wreck the barrier.

Beyond coatings for printability and functional properties, the luxury packaging sector involves coating for decoration, which may be associated with embossing, hot-foil stamping and metallisation. Fancy paper bags are a example of an old packaging format, which has seen a renaissance as a 'designer' totem for the 'teen fashion markets with bags made from high basis-weight coated and coloured materials. The packaging of premium beverages, chocolates and cosmetics offer high margins for producers of specialty paper grades, but require flexibility in production technologies. The value of the product requires high levels of uniformity to avoid the risk of costly consequential losses.

## Converting vs end-use properties

Maintenance of the balance between competing physical properties is a problem not encountered in communication grades to the same degree. As an example, high out-of plane stiffness would be thought to be a desirable feature in folding boxboard of corrugated to confer pack rigidity. However, stiffness also equates to 'spring-back', ie resistance to folding into a 3-D shape. This causes problem in gluing the flaps and carton joints, since the spring-back force places strain on the adhesive film during bonding. Thus a hot-melt adhesive may be strained while still in a warm plastic state. The damage may not be evident until the carton is filled and placed in a freezer whereupon the joint fails.

The cure may lie in better scoring and creasing, or in reducing the sheet strength properties, eg lowering ply bond to allow better delamination in creasing and folding, and reducing bending stiffness. In effect, the uniformity of the internal bond in the Z-direction is deliberately perturbed to allow better folding and gluing(1).

Where an aqueous adhesive is used, surface wetting and coating absorbency are also issues that may require changes to coating formulation as well as base stock. The compromise here may be in optical properties or pigment binding power versus the absorbency of aqueous adhesives. The use of more porous binders, ie vinyl or styrene acrylics in place of SBR lattices, buys gluability at the expense of a higher binder: pigment ratio to preserve surface strength.

## Process and product uniformity

### Grammage, Strength and uniformity

The foundation of product uniformity lies in the sheet forming and coating processes. The origins of uniformity on the process were explored in the paper given by the author in the 2005 Conference(2) and embrace both surface topography and interior sheet structure.

In the context of coating, topography is developed from

- Surface microflocculation,
- Wire mark,
- Felt mark,
- Surface sizing and calendering.

The 'surface architecture' governs coating uniformity, gloss, smoothness and also coating composition(4). The net effect of coating is to remove the higher-frequency element of roughness amplitude and the larger diameter pores, and to alter the surface profile. The surface of the uncoated base stock resembles a plateau with sub-surface canyons, pits and depressions. The addition of coating converts this profile to one of gently undulating hills - *Figures 1 and 2.*

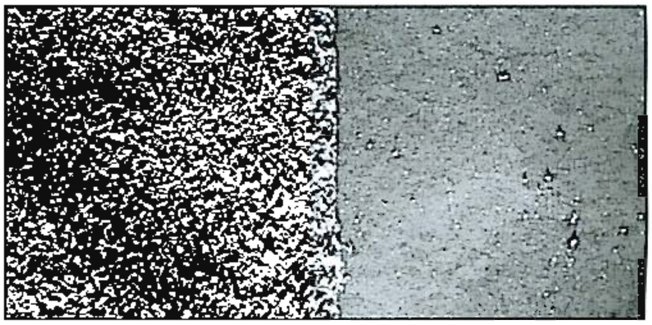

Figure 2 Uncoated and coated surfaces (pigmented coating)

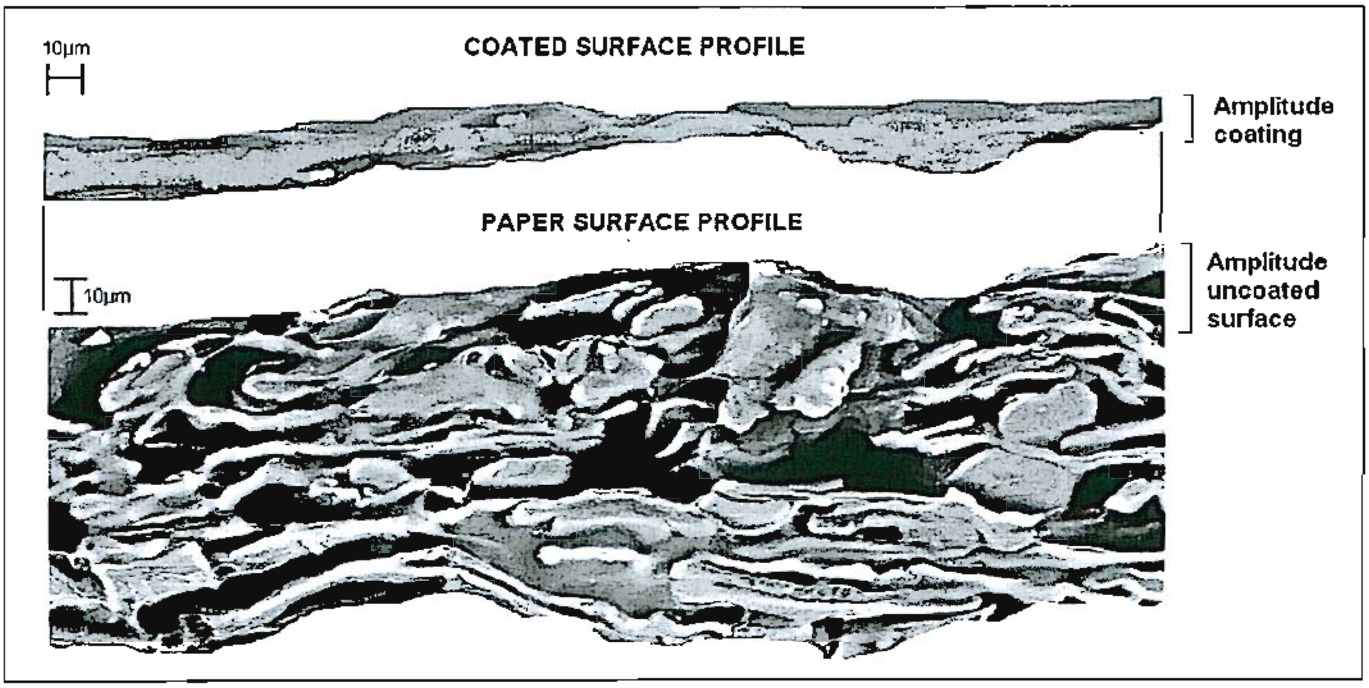

Figure 1 Uncoated and coated surfaces (polymer coating)

Print defects extend from ink gloss and ragged edges to dots at the micro-scale to mottle in solids at the macro-scale. Despite the reduction in surface frequencies and amplitudes, there may still be sufficient 'information' in the surface to interfere with the printed image that itself is based on the frequencies and amplitudes of the dots.

The base stock properties that determine coating performance are intimately linked to those that govern the mechanical properties of the board, ie the protective function of coated packaging is limited by the uniformity of the internal fibre network. The effect of the drive for lightweighting, described later, is becoming increasingly influential in terms of the uniformity-grammage-strength relationships. As basis weight is reduced, so the specific strength parameters, eg tensile or compressive indices also reduce(3). In practice, the strength index reaches a maximum at an intermediate grammage, then declines - *Figure 3.*

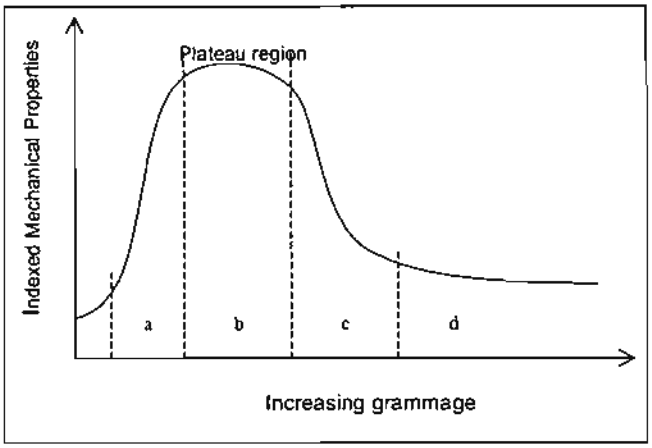

Figure 3 Strength index-grammage relationship (Source: C Sevajee)

At lower basis weight, there is insufficient fibre to transmit applied stress efficiently through the fibre network. At higher basis weight, there is an increasing amount of redundant fibre that plays no useful role in transmitting internal stress, but acts as a space filler, rather like the fluting layer in corrugated board.

**Uniformity, strength and basis weight - experimental**

Recently trials were made by Dr Christina Sevajee on the pilot paper machine at the University of Manchester under the aegis of a Knowledge Transfer Partnership (KTP) in order to look at the relationship between grammage, formation and strength(4). The following conditions were involved:

- Fibre source - 100% commercial recycled board
- Stock consistency - 2.5%
- Paper Machine - Fourdrinier
- Two headbox consistencies - 0.5 and 0.7%
- Grammage range - 30 to 200 $gm^{-2}$
- Physical properties analysed - Tensile strength, Elastic Modulus, RCT, SCT, Stretch
- Image analysis - Beta Radiograph, from which it was possible to obtain floc grammage and diameter values.

*Figure 4* shows the relationship between tensile index and grammage. Stretch and elastic modulus followed similar trends.

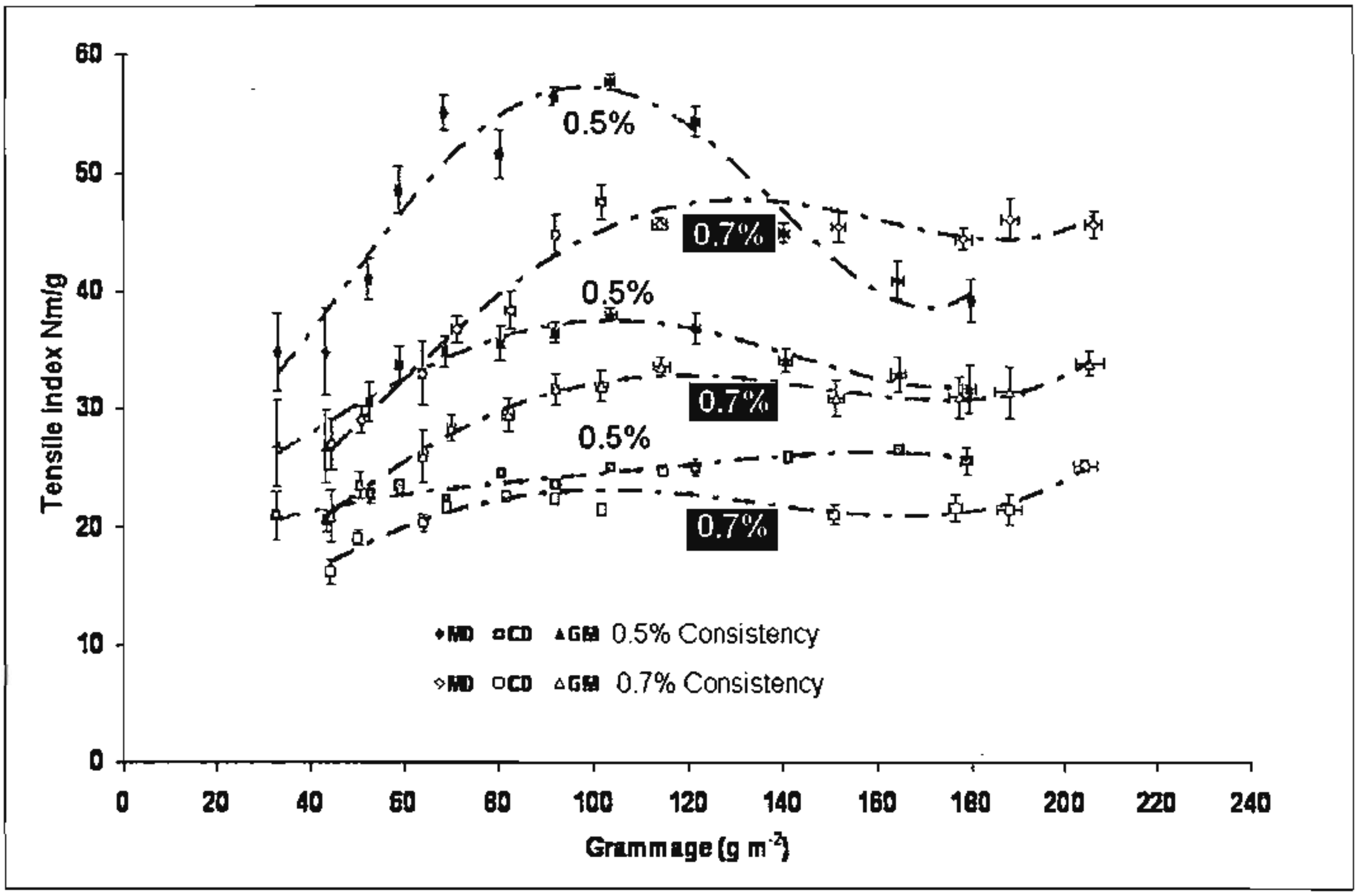

Figure 4 Grammage - tensile relationship

The MD values are larger than the CD ones, showing a high degree of fibre orientation. The effect of increasing the headbox consistency and therefore reducing formation uniformity was to both reduce the maximum values and shift the maximum to higher grammage as suggested before. From the coating perspective, the loss of base sheet uniformity at higher consistency would also undermine coating uniformity. *Figures 5 and 6* show the formation effects. The variability increases as consistency increases and as the level of resolution - the 'zone size' - reduces, *Figure 5*.

The images are renditions of the formation under different grey scales. The 'thin spots' at the higher consistency are plainly visible. The coating uniformity would suffer as a consequence leading to both print mottle and variations in opacity and gloss.

*Figure 6* shows variability in relation to grammage. Reducing consistency reduced variability overall but increased the rate of change of variability with reducing grammage, especially below 60 g/m².

This grammage range embraces not only single ply products, eg lightweight linerboard and heavier weight label and sack grades, but also individual plies in multiply box board grades. The middle ply is usually the dominant component in terms of fibre mass and effects on uniformity, but the outer piles are those with immediate contact with the fibre. The inner and outer plies will occupy different positions on the strength-formation-grammage relationship and the lower grammage outer plies may be more sensitive to shifts in forming conditions than the inner one, though the latter may have the greater effect on uniformity.

The results above are only drawn from one type of furnish on one, slow machine but the principle generally holds good. For example, low basis weight label stock made from a highly refined furnish with bleached hardwood content would tend to

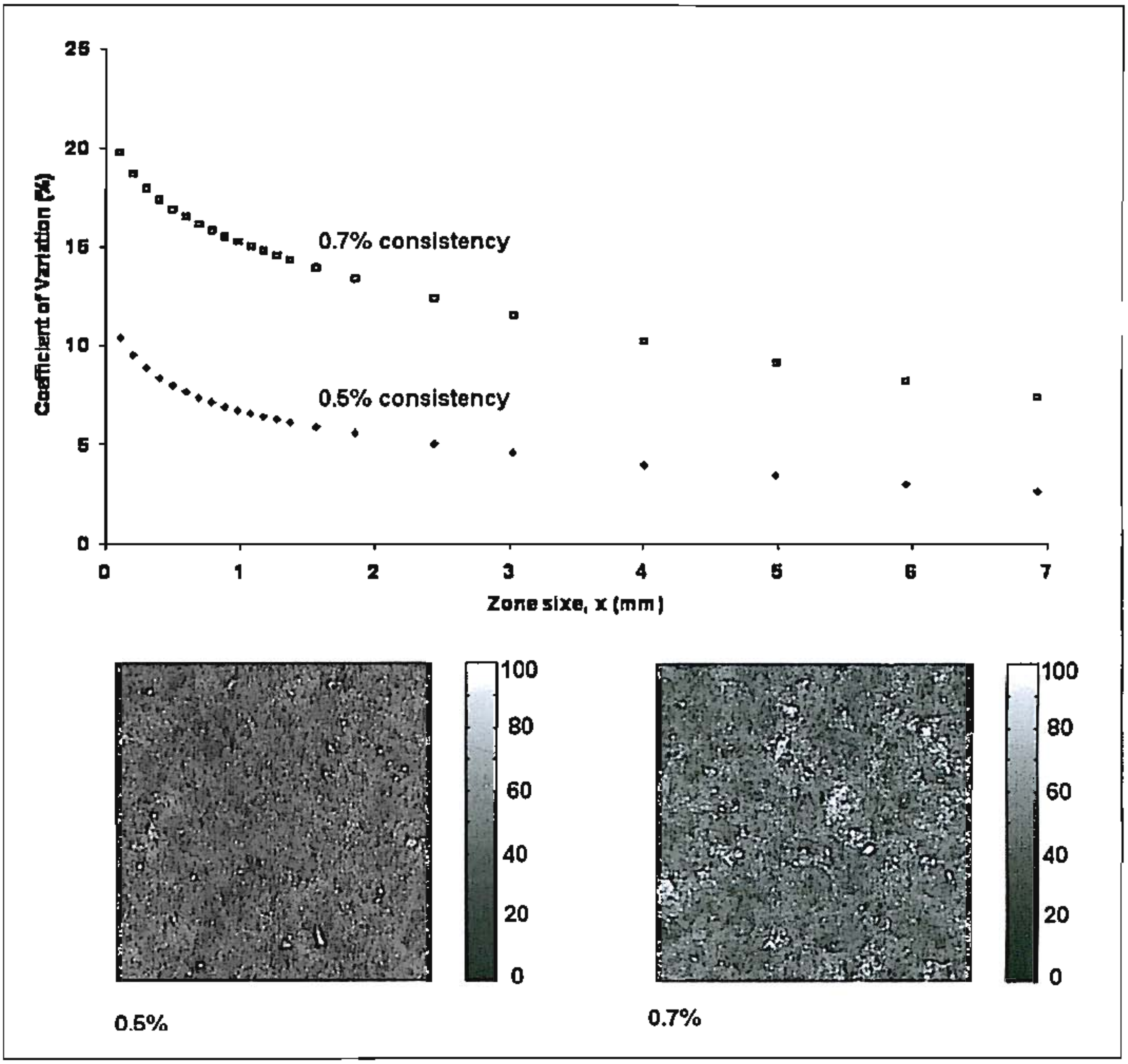

Figure 5 Formation variability vs level of resolution (after C Sevajee)

shift the variability trend to a lower grammage range. This would also hold good for the outer plies of multiply board.

**Scale effects**

Basis weight and sheet thickness may reduce, but the dimensions of the surface topography will not, hence for paperboard there will be a tendency for coatweight to increase as a proportion of total basis weight unless surface uniformity is improved. This not only increases costs, but also may lead to cracking at the fold.

**Furnish variables**

Ultimately, the grammage-formation-strength relationship depends on fibre properties(5), eg fibre coarseness, fibre length, and degree of fibrillation. To this may be added surface chemistry as determined by the pulping and/or bleaching process and the wet end additives. In integrated mills, the variability of fibre supply remains a key issue which is not always adequately monitored. The advent of automated and semi-automated systems for fibre monitoring will enable cause-and-effect relationships to be established for effects of fibre on sheet structure. From measurement comes control.

## Summary of effects

In summary,

- the coating uniformity is dependent on the uniformity of the base stock, both surface and interior.
- the same elements of sheet structure also determine converting and strength properties
- grammage, formation and strength properties are interconnected
- at lower basis weights, the strength indices reduce due to increase in variability of the sheet structure.

This latter point is very important when considering lightweighting in packaging products. As basis weight reduces, so the need for product and process uniformity increases with a requirement for more sophisticated control of the forming process as the foundation for coating. Other developments in technology and pack design will reinforce the requirement for uniformity. These are considered next.

## Future developments and end-user demands

The drive for lightweighting has already been noted. The EU countries are probably in advance of North America in this trend, under the impact of onerous packaging waste regulations. There are also economic influences - the need to reduce distribution costs of both packaging and packaged goods and the fact that paper and paperboard is bought by weight but used by the unit length. Lower basis means longer run length for the converter! Technologies that will demand greater product uniformity will include:

- Barrier and functional coatings,
- Digital print
- Radiation cure coatings, pre or post print
- Higher speed printing and converting lines
- Anti-counterfeiting
- Printable electronics.

In functional coatings, cost and recyclability require minimum coatweight, the more uniform is the substrate, the lower the practicable coatweight.

Digital print has been a 'long time a-comin', due to issues of speed and the capital, maintenance and running costs. However, it is establishing itself in specific product areas, notably CMYK printing of labels on narrow-web presses. For run lengths of 2000 metres, a speed of 16m/min is acceptable, as speed increases, so the economic run length will increase(6).

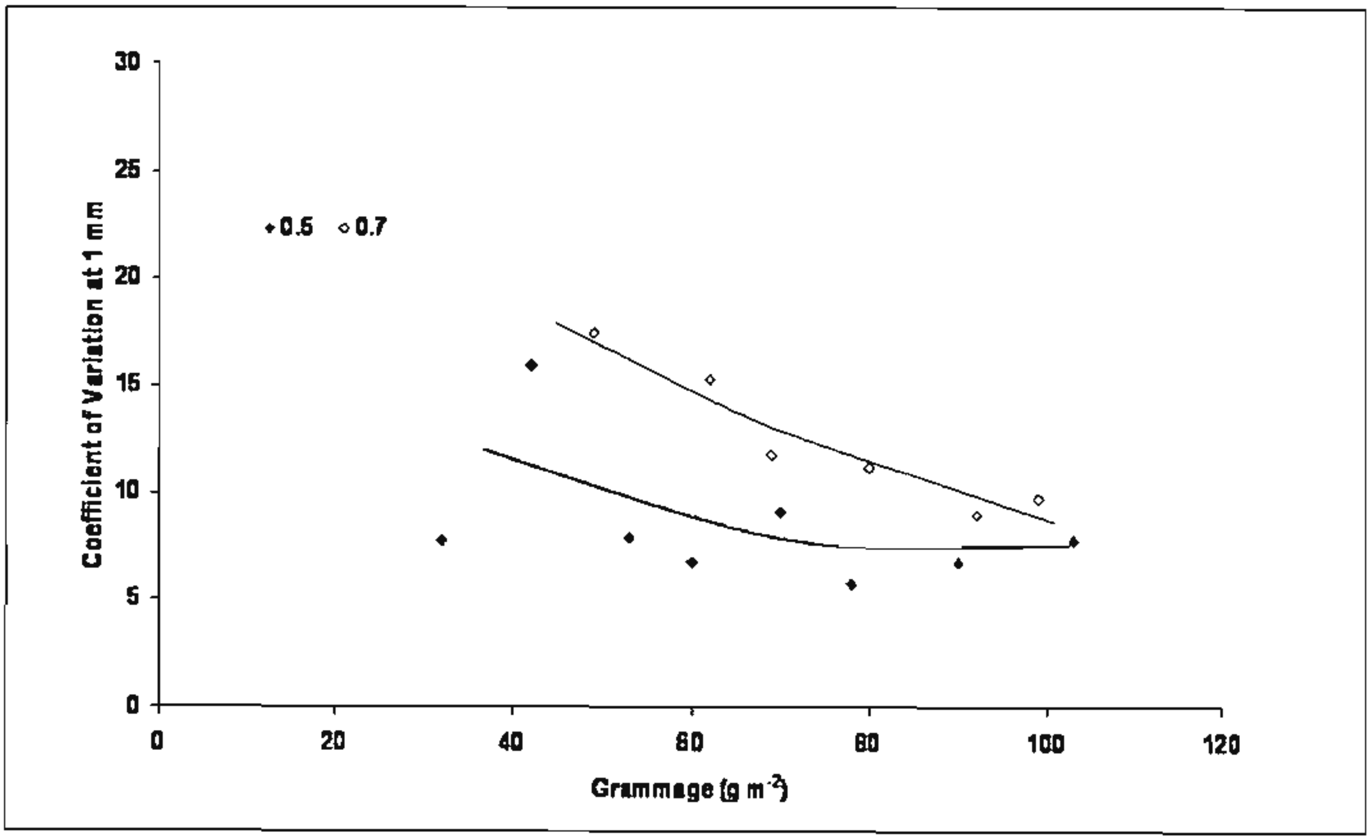

Figure 6 Formation Coefficient of Variation vs grammage (after C Sevajee)

Another area of digital development is in the printing of corrugated containers for consumer durables and point of sale displays where the size and value of the product dictates short runs and where digital print can compete in terms of short set-up time. Speeds of up to 6,000 sq m /hr are feasible. Such speeds will require tight control of substrate surface micro-structure(7) for accuracy in imaging.

UV curable inks offer greater speed of output and the ability to provide spot varnishing by inkjet, litho, flexo or gravure. Even offset litho has developments such as concentric screening systems where the dots take the form of concentric rings. The greater the width of the rings, the more is intense the colour. Such systems are claimed to reduce half-tone mottle and increase definition, but the frequencies involved may well pick up non-uniformities at higher levels of resolution. Electron bean cure is being installed on flexo printing and converting lines, especially in the US. This technology may raise questions about the chemical uniformity of the substrate due reactions between the electron beam and fibre or coating binder with the risk of odour and taint.

Speed is of the essence. The application of pressure sensitive labels and release stock can already be made at 1,050 labels/min. Speed will increase as older equipment is replaced by new installations. This doctrine applies to labels, folding boxboard, corrugated, flexible packaging etc. Higher speeds mean greater material demands in terms of tensile, stretch dimensional stability, stiffness etc.

Anti-counterfeiting measures will also require high surface uniformity of the substrate, eg, to avoid interference with concealed information patterns. An example is the application of laser-imageable coatings for authentication by the end-user. The most demanding application will be the printing of electronics. The coated surface will require a high level of precision for the layout of the components, eg UV curable metallic inks for antennae and conductive polymer inks for printable electronics - sensors for condition monitoring and diagnostics, photo voltaic cells, RFID tags, light emitting diodes. The applications extend beyond anti-counterfeiting or condition monitoring but to promotional devices - noisy, animated and scented packaging!

## Conclusions

- Coated paper and board products for packaging require uniformity not just in the coated surface but also in the physical and surface properties essential for end use. A balance also must be struck between end-use and converting properties.
- The common link between coating and strength properties lies in base sheet uniformity.
- There is a non-linear relationship between strength indices and grammage, with a maximum value and critical thresholds at lower and upper grammages beyond which, the strength per unit mass of fibre reduces.
- This relationship has implications for the lightweighting of coated packaging.
- Non-uniformity tends to increase as the spatial resolution diminishes, so a sheet may give low mottle in solids, but loss of definition in half tones when printed.
- Greater non-uniformity in formation reduces the strength indices in relation to grammage as well as reducing coating uniformity.
- The non-uniformity of the base stock extends all the way through wet end chemistry and sheet forming to the fibre supply.
- Future trends in packaging technologies will require higher levels of uniformity as well lightweighting - reduction of packaging mass.

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# Measuring and Evaluating the Surface Quality of Gravure Papers

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SESSION FOUR
PAPER NINETEEN

## Summary

Although nowadays a number of paper properties are determined using measurement technology, printers are still not always in a position to reliably predict the quality of a print. This is due on the one hand to the interaction of paper, printing ink and printing-related parameters and, on the other hand, to the fact that paper properties cannot be measured under practice-oriented conditions in the laboratory. An important fundamental paper property that greatly influences print results is the surface structure of the paper. This quality is also termed smoothness (roughness). Nowadays, smoothness is usually determined in the paper industry as surface smoothness using indirect measuring methods (air stream measuring methods). In addition to surface smoothness, the measurement of printing smoothness is very important, i.e. the determination of the surface structure of the paper under converting conditions.

Together with the rapid developments in computer technology, a number of topographical instruments have been developed that are capable of non-contact, direct measurement. These instruments are designed so as to be at least non-sector-specific, which means that they must be made useable for the applications in the paper industry on a case-to-case basis. The possibilities these instruments offer in describing surfaces will be discussed based on analytical results. One drawback of this technology, however, is that the surface topography is not determined under actual converting conditions (under applied pressure). This is only currently possible by using contact area testers that make it possible to operate at pressures ranging from 2.5 MPa to 7.5 MPa. As originally designed and built, however, these devices provide only an integral measured value for the surface finish. In order to remedy this disadvantage, an existing FOGRA contact area tester was therefore equipped with a high-precision distance measurement system and connected to a digital image processing system. The result of measurement is the development of the surface structure as a function of paper deformation under compression load.

This technology was used to measure eight natural gravure papers (SC papers) that had been gravure printed in a large print shop. The results were assessed by both direct visualisation and image analysis. The results of smoothness measurement were correlated with the print assessments. It was established that there is a strong relationship between surface structure, the deformation behaviour of the paper under load and the quality of the printed image. The best correlations were obtained for a newly defined parameter termed the $\mathrm{Grad(CA)}_P$.

## Introduction

Although it is currently possible to determine a number of paper properties using measurement technology, it is not yet possible to reliably predict two complex properties due, on the one hand, to the above mentioned complexity of the printing process itself and, on the other hand, due to the fact that paper properties cannot be measured under practice-oriented conditions in the laboratory.

An alternative means of evaluating printing quality is currently to make test prints or small-scale print runs. The resulting prints are then assessed either by direct visualisation and/or image analysis. This approach also involves technical outlay, however, and is therefore expensive. Moreover, it does not always produce clear results so that in-depth paper characterisation still rates highly.

The objective is to measure fundamental paper properties right on the printing paper produced - or even better to measure them during the production process - to be able to draw irrefutable conclusions regarding the printability of the respective paper *(Figure 1)*.

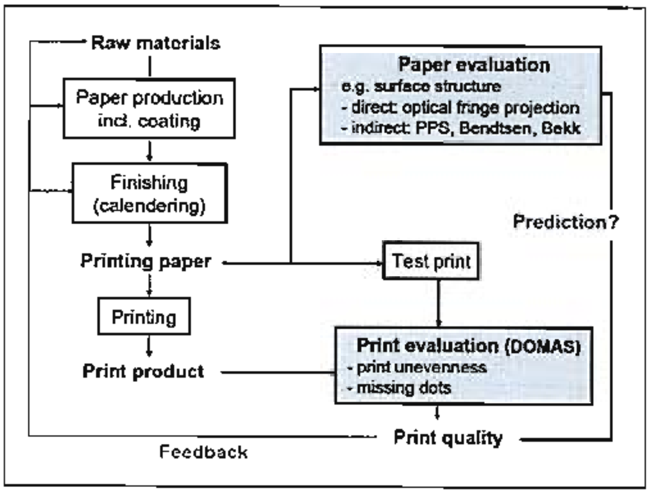

Figure 1 Problem definition

Within the scope of this study, the print results of eight natural gravure papers (2 SCA papers, 2 SCB papers, 4 superimproved newsprint papers) that had been gravure printed in a large printing works, were assessed by both direct visualisation and image analysis *(Table 1)*.

Papers A-F were printed in a first printing trial, whilst papers P1 and P2 were printed in a second printing run. The two trials are not comparable. *Table 1* illustrates some of the important basic properties and results of print assessment.

The full-scale prints were evaluated visually by comparing pairs of prints with respect to the following complex parameters: overall impression (Total), print quality in areas of low coverage (missing dots - MD) and print unevenness in solid areas (PU). The resulting paired comparison index is higher, the better the print quality of the sample is. In addition, the samples were measured using the DOMAS image analysis system which consists of a number of modules for print product evaluation. This makes it possible to analyse halftone dots. The printing parameter characterised as "DOMAS-MD" provides the number of missing dots / cm_ in the examined sample. In addition, the print unevenness in solid areas was examined by power spectrum analysis (PSA) based on structures contained in the printed image (DOMAS PU). The result is lower, the more uniform the printed image of the sample is. The latter applies as well to the formation index (FI) which DOMAS also analysed.

## Surface measurement technology

One important fundamental property of paper that greatly influences the print results is the surface structure of the paper. This quality is also termed smoothness (roughness). Smoothness constitutes a mechanical property and should not be equated with surface gloss (which is an optical property), although certain relationships between both parameters are evident, especially in the case of natural papers[1].

A number of smoothness measuring methods have gained market acceptance in the course of time and are generally subdivided into direct and indirect methods. The direct methods attempt to describe the surface geometry directly, whereas the indirect methods provide an equivalent parameter for smoothness that correlates with the surface, but which in turn is influenced by other parameters to a greater or lesser extent.

Nowadays, smoothness is usually determined as surface smoothness in the paper industry using indirect measuring methods. It can be safely assumed that in future this process will be superseded by direct smoothness measuring methods. Besides surface smoothness, the measurement of printing smoothness is also very important, i.e. the determination of the surface structure of the paper under converting conditions. Appropriate measuring instruments (Chapman tester, FOGRA contact area tester, Pira printing smoothness tester) have been developed that make use of the structure-induced difference in reflection behaviour of a paper pressed against a glass prism. A serious drawback of these devices is that they only provide an integral measured value.

*Table 2* provides an overview of the smoothness measurement methods that exist in the paper industry according to VOLK(2).

The method and results of two surface measurement methods will be discussed below. The first method discussed is a non-contact optical measuring method that makes use of digital strip projection, whilst the second studies involve the use of a modified FOGRA contact area tester.

| No | G | $m_A$ | ρ | FC | FI | Print quality | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | g/m² | g/cm³ | % | (PSA) | Visual - PV index | | | DOMAS | |
| | | | | | | Total | MD | PU | MD | PU |
| A | INP | 51.5 | 1.01 | 35.0 | 415 | 60 | 20 | 44 | 5.06 | 31.6 |
| B | INP | 51.8 | 1.08 | 35.1 | 367 | 116 | 120 | 184 | 2.31 | 16.6 |
| C | SCB | 51.8 | 1.04 | 32.1 | 358 | 80 | 168 | 88 | 1.69 | 27.4 |
| D | INP | 52.0 | 1.06 | 34.9 | 400 | 60 | 16 | 8 | 6.44 | 35.8 |
| E | INP | 52.1 | 1.11 | 35.9 | 360 | 72 | 140 | 80 | 1.38 | 29.6 |
| F | SCB | 52.2 | 1.13 | 37.8 | 221 | 156 | 120 | 180 | 1.25 | 20.9 |
| P1 | SCA | 55.9 | 1.19 | 38.6 | 229 | | | | | |
| P2 | SCA | 55.3 | 1.18 | 37.3 | 268 | | | | | |

| | | | |
|---|---|---|---|
| G | Grade | Total | Overall evaluation |
| FC | Filler content | MD | Missing dots |
| FI | Formation index | PU | Print unevenness |

Table 1: Paper grades, properties and printability

| Indirect methods | Direct methods |
|---|---|
| **without measuring pressure** | |
| - Gloss meter<br>- Capacitive instruments | - Laser profilometry<br>- Digital strip projection and coded light techniques<br>- White light interferometry |
| **with measuring pressure** | |
| - Air leak instruments<br>(Parker Print Surf, BEKK, Bendtsen)<br>- Friction tester | - Mech. sensing profilers<br>- Contact area measurement |

Table 2: Overview of smoothness measuring methods

## Digital strip projection - direct topography measurement without measuring pressure

A modern, non-sector-specific optical measuring technique for surface characterisation is digital strip projection coupled with the acquisition and evaluation of an image sequence based on the phase shift method or a combination of the phase shift method and coded light techniques. This measuring technology allows 3D height images to be generated which can then be used to determine in a quick and reproducible manner the surface parameters defined in DIN EN ISO 4287-1998(3).

*Figure 2* illustrates the sequence of operations involved in acquiring topographic parameters. As indicated in the camera image *(Figure 2/1)*, a series of strip patterns is projected on to the surface of the paper to be evaluated and scanned by a CCD camera. Software is used to calculate the topographic strip deformation and create a height image. Starting with the unfiltered height image *(Figure 2/2)*, the topographic parameters are determined in basically the same way. First of all, the unfiltered height image (raw data) is aligned so as to compensate for deviations in the parallelism (inclined or slanted position) of the paper and image planes. The result is illustrated in *Figure 2/3*. The primary information is subsequently broken down into detailed information such as waviness and roughness by the use of filters (e.g. a wave filter in compliance with DIN EN ISO 4287-1998). The result of such high pass filtering is shown in *Figure 2/4*. The fifth step then involves calculating different topographic parameters such as Ra, Rz, Rq.

*Figure 3 (next page)* again illustrates in detail the separation of information from the primary profile into long-wave (waviness) and short-wave (roughness) shape deviations based on a cut-off wavelength. The result of topographic parameter calculation is highly dependent on the cut-off wavelength and other filter settings so that, if results are to be highly reproducible, these values must always be cited as well.

There might at first be some speculation about whether or not individual topographic parameters are suitable for predicting certain usage properties such as print results. The fact is, however, that most of the calculated parameters originated in the field of metal technology and thus have only limited relevance as far as the behaviour of paper is concerned. An intensive familiarisation with the field of metrology and the mathematical basis of the calculated topographic parameters, however, is absolutely essential before finally introducing this technology to in-house use. It is often reasonable to test the suitability of individual parameters in a defined manner using a selection of different papers. The surfaces of the papers will then be considered as different manifestations of functional surfaces, e.g. "smooth", "slightly rough", "very rough", or classified according to a printability parameter. It is then a matter of selecting those parameters that best correspond to this classification. Non-linear relationships are also feasible in many cases. The parameter found and the corresponding model correlation must then be scrutinised critically.

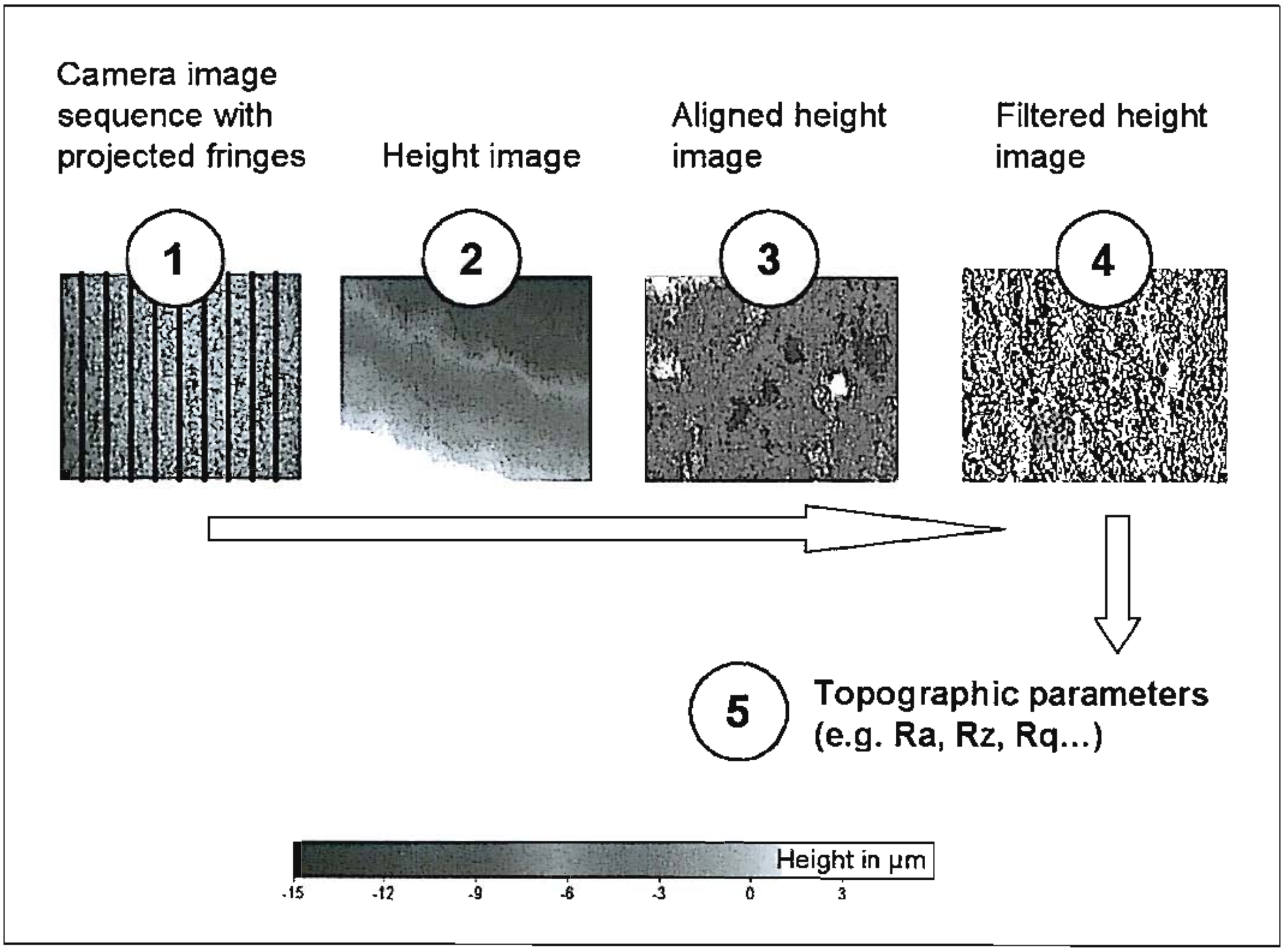

Figure 2: Image acquisition

*Figure 4* shows the results of the first printing trial (papers A-F) in the form of missing dots per cm² plotted against core roughness $S_k$. The measurements were conducted with a MicroCAD system manufactured by GF-Messtechnik (Teltow, Germany). Measurement was carried out with a horizontal resolution of 8 $\mu$m and 24 $\mu$m with a 3x3 pixel filter and a vertical resolution of 0.8 $\mu$m. The size of the area to be measured was 9 mm x 12 mm. A wave filter with a cut-off wavelength of 1 mm was used to filter the height images.

If paper C is left out of consideration, it might be concluded with high statistical significance that the number of missing dots increases exponentially as core roughness increases. Paper C, on the other hand, showed only few missing dots per cm² although it exhibited high core roughness.

*Figure 4* clearly demonstrates that we must refrain from thinking that we can generate a comprehensively conclusive prediction of printability results solely by measuring smoothness. On the contrary, it is necessary to examine other paper properties such as compression, penetration, porosity, etc. and their interactions when pressure is applied.

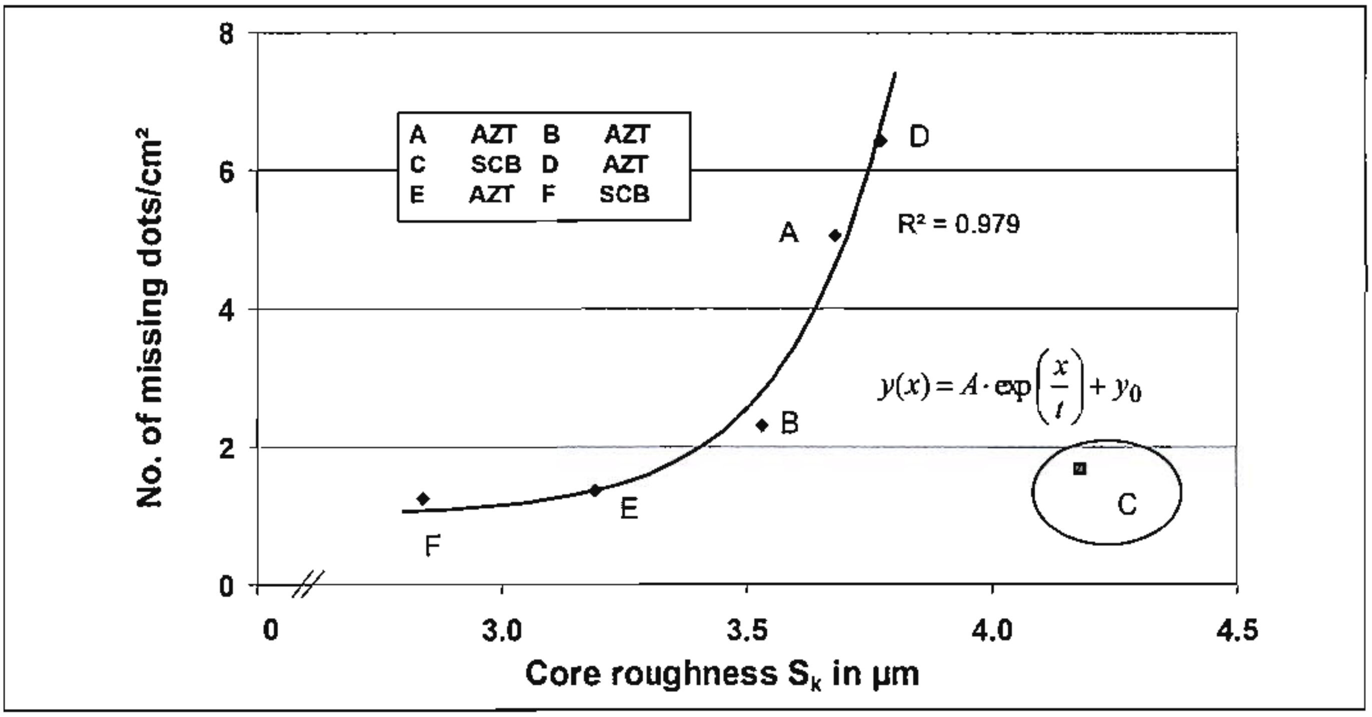

Figure 4: Core roughness $S_k$ - missing Dots

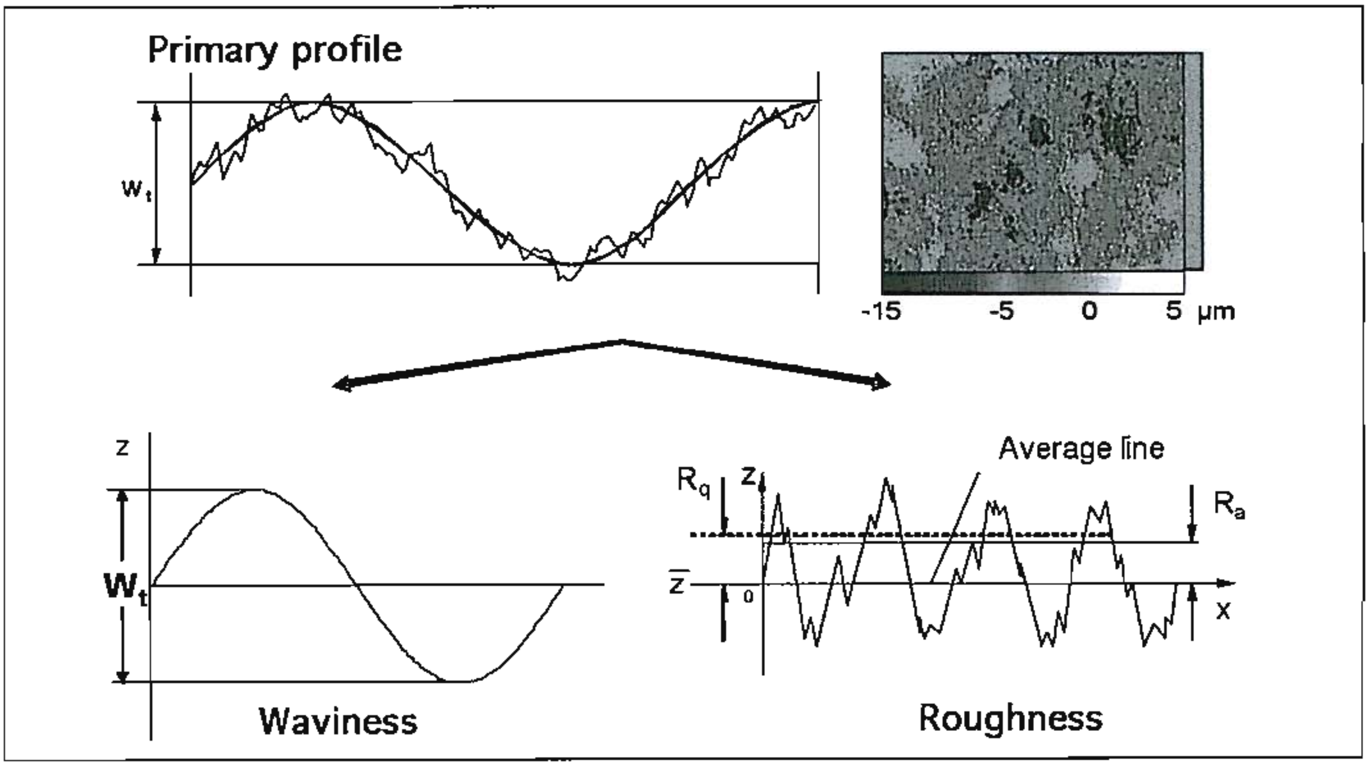

Figure 3: Data filtering

In addition, it must be noted that the topography measurement described above was carried out under non-pressurised conditions, i.e. the deformation of paper, which in industrial converting is either unavoidable or perhaps even desired, was not taken into consideration.

## Modified FOGRA optical contact tester - direct pressurised surface structure measurement

The FOGRA optical contact tester has existed for several decades and is well suited to evaluate the surface structure of papers under load. An existing FOGRA optical contact tester was equipped with a high-precision distance measurement system and connected to a digital image processing system. This made it possible to obtain additional information about the reaction of paper volume and paper surface above and beyond the integral quality parameters of the contact area that have long been traditional in the paper industry.

The simultaneous digital measurement of the contact area, the pressure applied, the deformation of the paper and the synchronised detection of contact area images (greyscale images) make the development of the surface structure in the form of the contact area as a function of the paper deformation under load available as a data-image matrix. This database allows paper compressibility to be calculated based on the thickness reduction as a result of load on the one hand. On the other hand, the database provides information relating to the speed and uniformity of the reaction of the paper surface during the printing load based on the spatial coordinate-dependent contact area values. *Figure 5* shows a basic schematic drawing of the modified FOGRA optical contact tester.

During the measurement process, a pressing die presses the paper sample vertically against a glass prism. The total number of areas of contact is then counted. The number of points of contact will be higher, the softer and smoother the paper sample is. One speaks of optical contact when the gap between the glass prism and the paper sample is equal to or less than half the wavelength of the light. In physical terms, this means a disruption of total reflection and thus a drop in the signal being measured. This is determined by a photoelectric receiver as the amount of light measured at the angle of total reflection. The contact area, expressed in per cent, includes all those areas in the sample that are in optical contact with the glass prism based on the total surface area measured. The measuring set-up makes it possible to look at the measured surface in a vertical direction from above. When viewed in this way, the observer sees the contact areas as bright regions and the non-contact areas as dark regions(4). The integrated optical distance measurement system functions in a contact-free manner and makes it possible to determine paper deformation with a resolution of

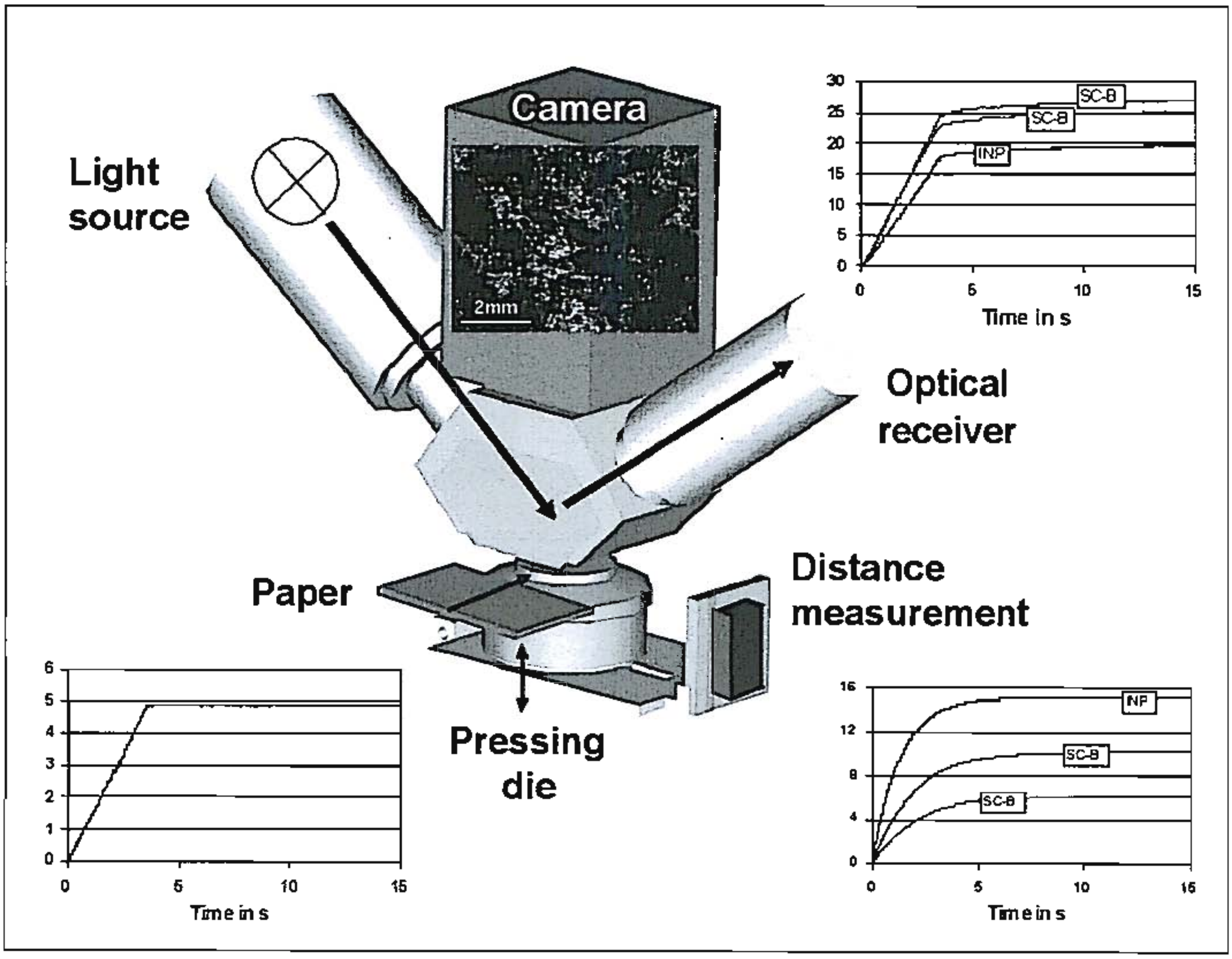

Figure 5: Modified contact area tester

better than 20 nm. Taking all device components into consideration, it is possible to measure deformation to an accuracy of 1.5 $\mu$m.

*Figure 6* shows by way of example the time-dependent progress of paper deformation for three of the sampled papers. Pressure build-up begins at t = 0 s, attains a pressure of 5 MPa after 3.6 s and is then maintained at a constant level. The rapid paper deformation at the beginning of pressure build-up is very obvious. But even after the final pressure has been attained, deformation of the paper continues to occur and is known as flowing. The deformation curves shown in *Figure 6* differ considerably in the maximum final deformation that is achieved. As might be expected, this material flow not only causes continued overall deformation of the sample, it also has a considerable effect, as it acts to change the surface topography. This is illustrated by the two contact area images in *Figure 6*.

Although this semistatistical analysis of the deformation processes on a time scale of seconds is of great interest in understanding the reaction of paper as a whole, it is insufficient to make reliable predictions about the phenomena that occur in the surface structure as it passes through the printing nip, since it must be assumed that the time of passage is less than 5 ms in this case. In order to approximate this time response, the functional relationships between contact area (CA) and pressure (p) as well as contact area and overall paper deformation were described mathematically based on measured data and then processed analytically.

The first derivation at location p = 0 MPa of the contact area development over pressure is defined as the parameter $\mathrm{Grad(CA)}_p$. It describes the initial reaction of the paper surface during pressure build-up *(Figure 7)*.

The value of parameter $\mathrm{Grad(CA)}_p$ is higher, the more the paper surface reacts during pressurisation by enlarging the contact area. Paper C has high core roughness and exhibits a high deformation potential of its surface during this procedure. This apparently results in a smaller number of missing dots *(Figure 8)*.

The following findings regarding the reaction of the paper sample to pressure can be formulated using the modified FOGRA optical contact tester. On the one hand, information can be derived pertaining to the overall deformability of the sample under semi-static conditions or by gradient formation at the time of pressure build-up. On the other hand, evaluation of the contact area images yields findings regarding the manner and speed of surface deformability during pressurisation in conjunction with distance and time co-ordinates. A metrological study of the papers during pressurisation makes it possible to correlate all measured papers - something that cannot be done in the case of non-pressurised measurement.

The results show that the old familiar demand for a "soft and smooth" paper for gravure printing remains valid, although it rather refers to the flexibility of the surface. Furthermore, addi-

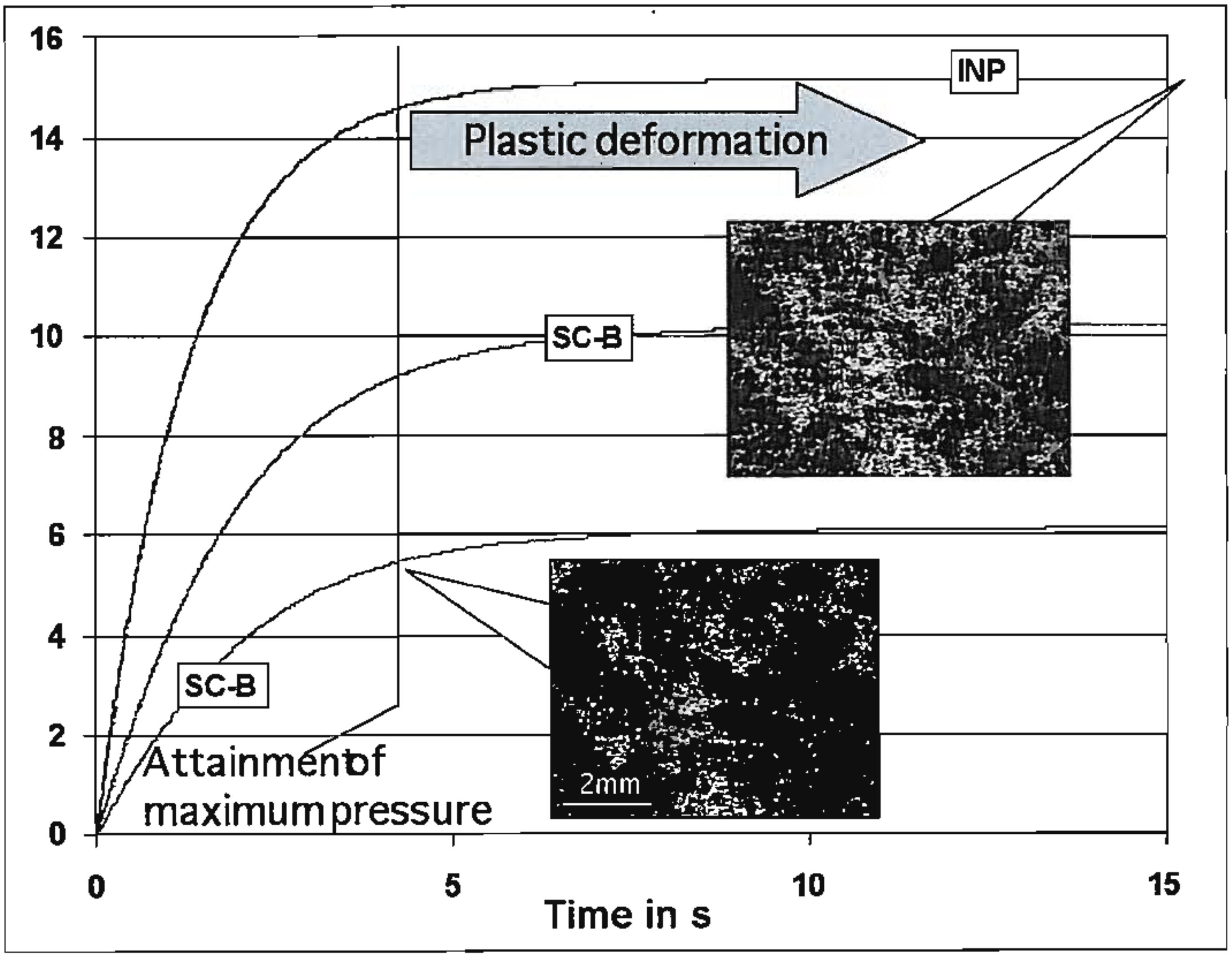

Figure 6: Contact area of gravure paper

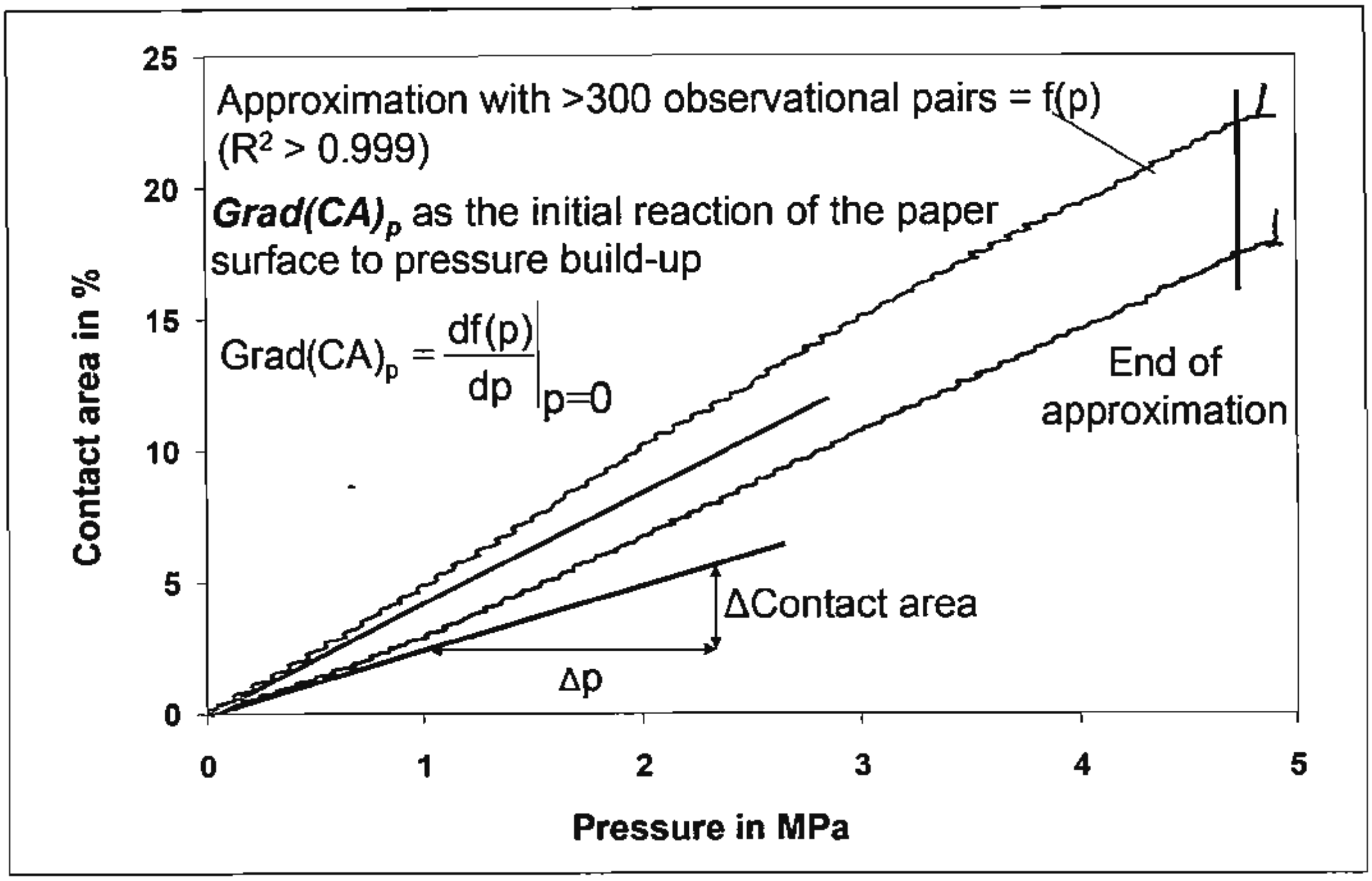

Figure 7: Definition of the parameter $\mathrm{Grad(CA)}_p$

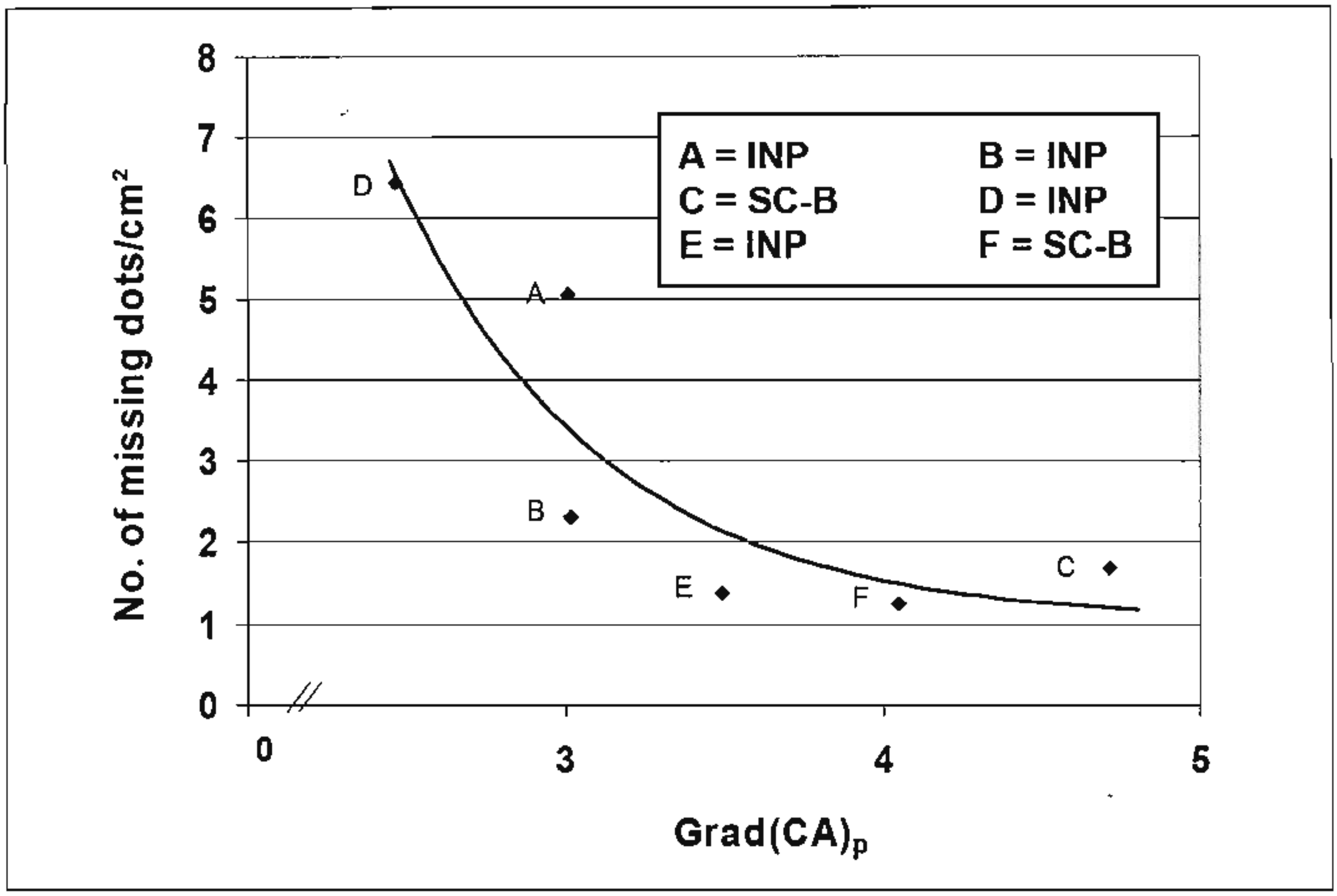

Figure 8: Printability - $\mathrm{Grad(CA)}_p$ - gravure paper

tional gradient formation revealed that the prerequisite for a good printed image (few missing dots) is a high ratio of surface structure change to overall compressibility. In addition, overall compressibility at a given contact pressure should be small, i.e. surface deformability is far more important for good print results than compressibility *(Figure 9)*.

*Figure 10* shows contact area development as a function of paper deformation.

After a rapid increase in contact area and deformation until maximum pressure is attained, the curves then pass into an area in which the contact area develops in almost linear fashion as deformation increases. The final portion of the curve is characterised by a faster increase in contact area.

In the case of papers A, B, D, E (improved newsprint papers), the deformation that occurs in the third segment is so marginal that, almost without exception, paper flow reflects the increase in contact area. The SC papers reveal greater increases in deformation in this region. It is assumed that the surface of the SC papers has a greater deformation potential (more flexible fibres) due to the greater proportion of virgin fibres in the SC papers.

The documented modifications of a FOGRA optical contact tester bring about an enormous expansion in the possibilities for describing both the total deformation and surface deformation of papers under compression loads. The potential offered by greyscale images that can be analysed as well has not yet been utilised completed.

At present, such modifications of the instruments have not yet resulted in any sort of standardised topographical parameters. The development of such parameters under compression loads would be useful and meaningful in this context.

## Summary

Proceeding from the realisation that conventional air stream measuring methods for surface characterisation could not establish a clear correlation between smoothness as a paper property and the printability results, two direct surface measurement methods for topographic evaluation of papers were chosen and compared with respect to their validity regarding the expected missing dots in full-scale printing.

Non-pressurised measurement according to the principle of digital strip projection quickly produces reproducible results that characterise the printability behaviour of most papers.

This method, however, came up against limiting factors in view of the fact that it is possible to characterise paper comprehensively only under real converting conditions. This lack of practical orientation was greatly reduced by modifying the FOGRA optical contact tester, thus making it possible to correlate the printability results (missing dots) of all papers tested.

All in all, the following findings regarding the printability results (missing dots) can be derived from the trials that were conducted:

- the surface must have good deformability properties (high value for Grad$(CA)_p$),
- the overall deformability of the sample should be low, i.e. the pressure energy should be used to deform the surface and not to deform the entire structure.

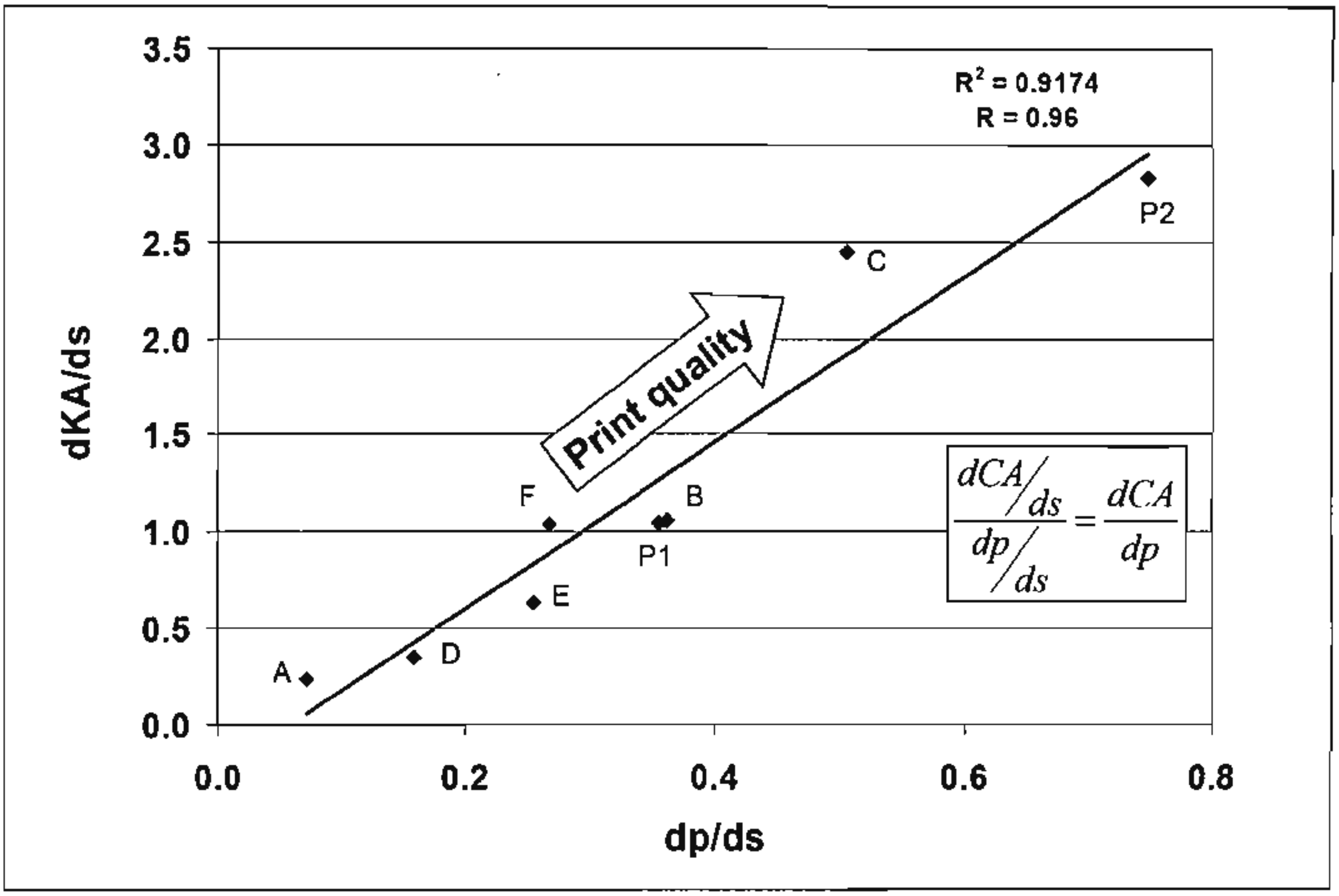

Figure 9: Initial reaction of paper during pressure build-up

Direct measurement methods are capable of providing a large number of topographical parameters in a quick and reproducible manner. This, however, does not necessarily mean that the absolute values can be compared with one another or even with conventional air stream measuring methods in each and every case. This in turn suggests that the introduction of such systems under conditions that prevail in practice will require preparatory work aimed at providing an understanding of the measured values. The extent and scope of such preparatory work should not be underestimated.

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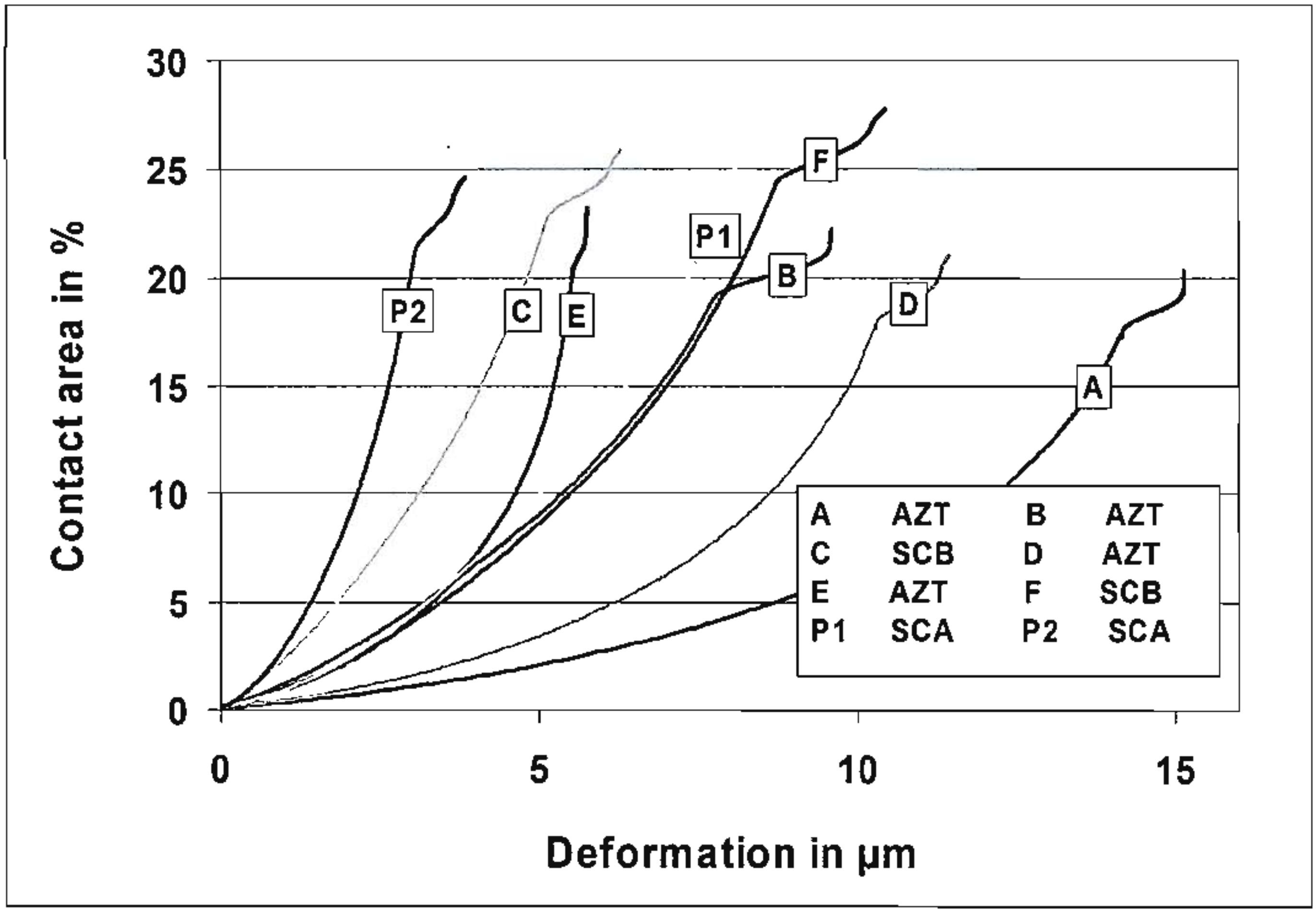

Fig. 10: Contact area = f(Deformation)

# NOTES

# A Re-evaluation of Factors Controlling Print Rub on Matt and Silk Coated Papers

by
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SESSION FOUR
PAPER TWENTY

## Abstract

Print rub, or ink scuff, remains one of the greatest challenges for the successful development of matt and silk matt offset coated papers. Using a recently proposed method for evaluating print rub, involving a non-slip pressure and friction-induced stress contact between a printed and unprinted sheet, this work seeks to test a newly-formulated hypothesis that the ability to improve print rub resistance is a function of coating surface capillarity (absorption) and adsorption properties, in combination with the roughness and compressibility/conformability of the basepaper-coating composite on the fibre-floc scale. A series of coated papers have been tested, ranging from woodfree single to multicoated grades, including the evaluation of compressibility and stretchability under pressure and shear both individually (pre-rubbing), to simulate external real-up, calendering and converting processes, and in combination with the aged and conditioned printed surface. The findings are used to illustrate the corner points of an hypothesis, from which is deduced that the most resistant surface to print-rub is a combination of high capillarity and high surface area of the pigmented coating, aiding absorption and adsorption, together with a uniformly compressible basepaper-coating composite structure, such that contact shear forces are minimised. Under conditions of compromise, such as a coating surface exhibiting low capillarity, an incompressible/non conforming sheet can help reduce print rub due to minimised contact area. The evidence tends to suggest that a too rigid coating-basepaper combination, such as developed by many modern paper machines together with multi-coating, is exacerbating performance difficulties in this paper sector.

**Keywords:** print rub, ink scuff, ink setting, print rub test, ink-surface interaction, printability, matt paper, silk paper.

## Introduction

The expanding market for matt and silk grade coated papers, together with the desire for ever higher opacity, bring challenges of compromise between optimal light scattering, mattness and printability. The parameters when optimised for each separate function are themselves not compatible with the other functions. For example, it is well known that maximum light scattering from a porous coating network is achieved when the particle size and the voids between the particles approximate to the wavelength of light used to view the paper. Typically this leads to an optimal average number particle size for, say, calcium carbonate of ~ 0.2 $\mu$m. To achieve uniform void size, the particle size distribution is frequently made as narrow as possible aiming at a monosize pore size distribution. This idealised light scattering scenario is, however, in stark conflict with printability, while a monosize pore size distribution with high connectivity leads to a highly permeable surface with low levels of capillarity. This means that, for example, thin varnishes and lacquers drain too readily into the paper or board surface, whilst offset paste inks fail to proceed to complete setting due to low capillary forces insufficient to draw resin-solving oils from the ink, resulting in a lack of print structural integrity and, in some cases, water interference-induced piling on the press. Furthermore, pigments with narrow particle size distributions are generally of low surface area, resulting in insufficient polar adsorbing surface for promoting chromatographic separation of ink oils[1] and ultimately for resin adsorption to take place - the result being poor ink-coating adhesion under conditions of high tack force[2,3] or under the application of contact pressure and applied in-plane strain as may occur in the finishing stages of binding and delivery of the printed format. This conflict of optimal particle and pore size distributions applies equally to gloss papers as to matt and silk finishes.

Matt and silk papers, by definition, have a microrough surface. This is essential to achieve optical mattness and sheen uniformity. The corollary of this microroughness is that the pigments used to achieve it are relatively coarse and therefore pack together to generate permeable coatings with relatively large pore sizes, $r$. Like the steep particle size distribution pigments discussed above, the large pores derived from coarse pigments also have low capillarity, i.e. low capillary pressures, $P$, according to the Laplace equation,

$$P = -\frac{2\gamma_{LV}\cos\theta}{r} \tag{1}$$

where $\gamma_{LV}\cos\theta$ is the surface wetting tension (contact angle $\theta < 90°$) between the liquid and the surface material of the pore, derived from the surface energy relationship of the liquid-vapour interface ($\gamma_{LV}$) and the energy of the surface. Matting pigments also have low specific surface areas. These conditions combine to give low capillarity, poor ink adhesion and limited ink resin adsorption. Solutions to overcome these problems, using specialised pigments of either high surface area (nano surface features arrayed on micro particles[3,4]) or by combining polar and lipophilic surfaces together in a carbonate-talc costructure[5], have been proposed.

Much of the previous work in the mechanistic study of print rub has concentrated on the abrasive properties of the paper surface as a potential parameter responsible for print rub. However, no clear correlations over a sufficiently universal sample set can be confirmed from this body of work[6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22], indicating that other mechanisms must be at play, such as those discussed above. The situation remains, as a result, that commonly used test methods for print "abrasion" are exactly what they say they are - tests for print abrasion as either a direct or indirect function of surface abrasivity. If correlation between print rub and the abrasiveness of the paper or board surface is poor, then so will the correlation fail between these laboratory tests and practice. On this basis, the work of Gumbel[23] conclusively showed that the test parameters required to form better correlation with practice are pressure between the printed sheets and applied lateral strain, which may or may not result in shearing of the ink, but certainly results in stress within the ink layer and at the ink-surface boundary. The author goes on to state that rub resistance is a most complex term, which is variously described as insufficient drying, strong carboning or lacking rub resistance. He continues by stating that all terms refer to the same problem: transferring printing ink under mechanical stress to white, impression-free paper surfaces.

Firstly, let us outline briefly a method for print rub evaluation described by Gane *et al.*[24]. The technique is constructed and applied on the Ink Surface Interaction Tester (ISIT), in which strain is applied to the ink layer during the passage through a nip under pressure during rotation of a printed sheet in contact with an unprinted sheet. The method has been extended in this work to investigate the effect of pre-compressing and shearing the unprinted surface on the subsequent print rub, as might occur during a variety of calendering applications, real-up, pre-converting etc. The results from these techniques, having been applied to a series of papers, including woodfree single and multicoated grades, are then used to verify a novel combined hypothesis, that print rub resistance is a function of coating layer capillarity and adsorption potential, i.e. a function of the number density of fine pores in the coating pore network driving the process of ink setting and their surface chemistry, and the basepaper-coating composite compressibility and conformability under pressure and shear, combining each to increase the ink back-transfer resistance and to reduce the stress induced on the ink layer under shear, respectively.

## Method Design

The simple rotational action of a printing nip forms the basis of the test design[24]. The usual compressive action of a nip provides mainly normal forces to the paper surface. In fact set-off tests are based on such a principle, in which a printed sheet is brought into contact with an unprinted sheet and the ink transfer, as a function of setting time, is measured via the parameter of transferred ink print density. The difference between ink rub and set-off, however, is the application of strain in the case of print rub. For example, the most common source points for print rub occur during cutting, trimming, binding and transport of printed stacks or finished articles. During such processes, lateral strain is often involved while the surfaces are pressed together. This leads to a shear stress in the ink film which can either deform plastically (smear) or break away from the coating surface under a viscoelastic response (post tack adhesion failure (Gane *et al.*[2]) if the resin is not fully hardened or fails to adsorb (adhere) onto the coating surface, respectively. Ink adhesion can be tested separately according to the methods of Gane *et al.*[2] and illustrated by Haenen[25] and Gane[26]. The key to a suitable print rub test, therefore, is to introduce the strain factor into the typical set-off method.

The compression under rotation in a nip is simply controlled by setting the normal force to a chosen value. On the ISIT this is applied and adjusted by a cantilever and spring arrangement. The normal printing pressure force is typically set to 50 kgf (~ 500 N) applied via a rubber covered printing disk (IGT type – rubber coated printing disk (2 cm wide) and this is used to apply a distributed ink layer (~1 gm$^{-2}$) at a printing speed of 0.5 ms$^{-1}$ to the test surface consisting of the coated paper sample attached to the rotating sample platen by double-sided adhesive tape (Tesofix 4961 colourless 25 mm x 50 m). The ink used in the tests described here was a "stay-open" duct fresh ink, Skinnex Cyan 4 x 73. After printing, the sample can be left for a chosen length of time - this can be varied according to the ink and the expected interval before converting, which in contemporary printing shops is becoming ever shorter.

The actual print rub test apparatus involves some relatively minor modifications to the instrument. A metal roller was fashioned of dimensions similar to that of the standard print roller. Metal was chosen to avoid the deformation impact of a typical printing disk rubber surface and its viscoelastic response that might lead to an unpredictable stretching of the paper surface during the test. The external protruding hub surface of the roller was coated with resin to achieve a high coefficient of friction to material contacting the outside of the roller, *Figure 1*. This is then mounted in the normal way on one of the print stations.

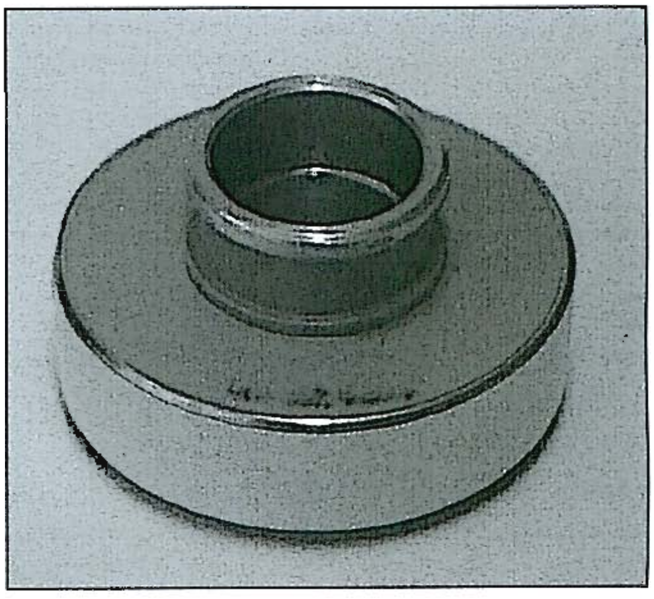


Figure 1 Metal disk matching a print disk design with a resin coating applied to the external protruding face of the hub and side surface to achieve a high friction coefficient. The unprinted contact strip is applied to the surface by double-sided adhesive tape.

To achieve an applied strain during the subsequent nipping procedure, a brake mechanism has been constructed so as to provide a torque against the direction of rotation. This was achieved by means of a coil spring extended to a known applied force and attached to a PVC-coated flexible loop which couples with the resin coated printing disk hub to provide a pre-determined braking torque via the coupling action of the coefficient of friction, *Figure 2*.

**Providing the strain via the braking torque**

The extension of the coil spring used to apply the friction force was maintained within the linear Hooke's law regime. The spring constant, $k$, was determined prior to mounting on the machine simply by applying known weights, $\mathbf{F}_{\text{spring}} = mg$, to the spring held vertically and measuring the extension, $\mathbf{x}$.

$$\mathbf{F}_{\text{spring}} = -kx \tag{2}$$

A convenient value for our experiments was found to be, $k = 50\ \text{Nm}^{-1}$. The adjustment on the machine was then made via the screw adjuster to a known extension and hence a known applied force. The practical force was chosen by trial and error based on the requirement that there should be maximum braking without inducing surface-to-surface slip at a nip pressure of 500 N, and was shown to be 7.9 N.

The coefficient of friction between the PVC-coated loop band, placed under tension by the extension of the applied spring, and the resin coated metal disk hub was then measured using a further spring extension experiment. This was achieved by attaching a further flexible inelastic band to the circumference of the mounted metal disk. A second spring of known spring constant was than attached to the band and extended until steady motion occurred. The extension force of this second spring, $F_{\text{pull}}$, at the onset of motion gave the effective coefficient of friction, $\mu$ (~ 2), by equating torques between the hub and the outer circumference according to

$$\mu = \frac{F_{\text{pull}} \cdot r_{\text{circumference}}}{|\mathbf{F}_{\text{spring}}| \cdot r_{\text{hub}}} \tag{3}$$

where the outer radius of the disk, $r_{\text{circumference}} = 3.40$ cm, and the inner hub radius, $r_{\text{hub}} = 1.55$ cm. The set torque being conveniently used was therefore at a value of ~ 0.25 Nm.

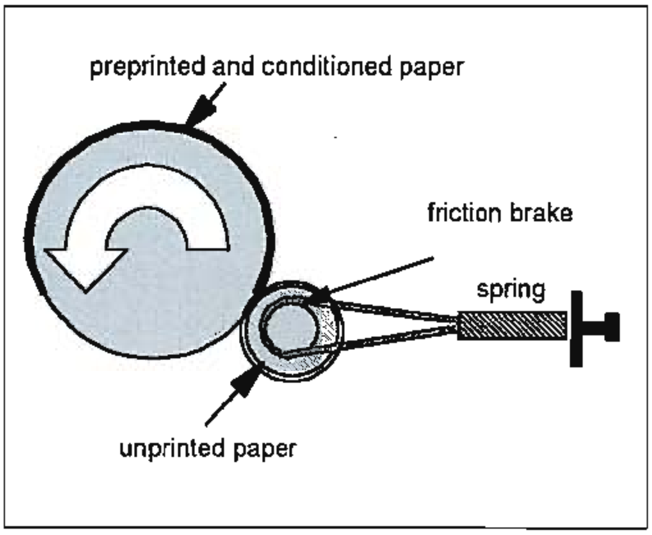


Figure 2 The application of a coil spring and PVC-coated flexible loop to apply a braking torque to the metal disk, shown both in practice and labelled schematically for clarity.

**Spectral analysis of transferred rubbed ink**

The transfer of print density after a chosen series of nips between the previously printed sample and a fresh unprinted surface of the same material mounted on the metal disk is measured over a spectral range suitable for the ink and paper being used. In our experiments we used a wide spectral densitometer range of 380 to 780 nm (according to DIN 5033 with D65 2°) measuring the remittance using a Techkon Spectrophotometer SP810λ at a resolution of 10 nm. The spectrometer operates with a high-resolution monolithic grating-diode array and delivers (besides XYZ and L*a*b* values) spectral information of the measured colour.

For a complete spectral analysis for actual print rub (ink transfer onto the unprinted sample) it is necessary to determine the difference between the remittance for the blank unprinted surface and that of the same surface after contact print transfer, as shown schematically in *Figure 3*. The results can be expressed using two convenient terms: (i) the difference in the maxima of the remittance spectra, $\Delta_{\text{at max}}$, taken as the difference at the point of maximum remittance, or dominant region, i.e. at the wavelength at which most radiation is returned to the detector (equivalent to the dominant wavelength associated with the substrate paper medium), and (ii) a transfer print "masking" density, $\Delta_{\text{at min}}$, taken as the difference at the point of minimum remittance, i.e. the wavelength range at which most radiation is absorbed by the ink, so "masking" the substrate background remittance. The value of $\Delta_{\text{at max}}/\Delta_{\text{at min}}$ might be used potentially to reflect the visual impact of marking.

**Test Procedure**

One of a series of strips of the paper or board sample is attached to the sample carrier platen, fixed with two small pieces of adhesive tape on both ends to ensure easy removal. The strip is printed with the standard IGT printing wheel, (in our case using the ink: Skinnex 4x73, with a print speed $0.5\ \text{ms}^{-1}$, applying 1 revolution at a nip pressure of 500 N). The sample is removed and allowed to "dry" for a chosen length of time (in our studies using the "stay-open" ink we allowed at least 48 hours or even up to a week). The aged dried printed strip is re-attached to the sample carrier platen.

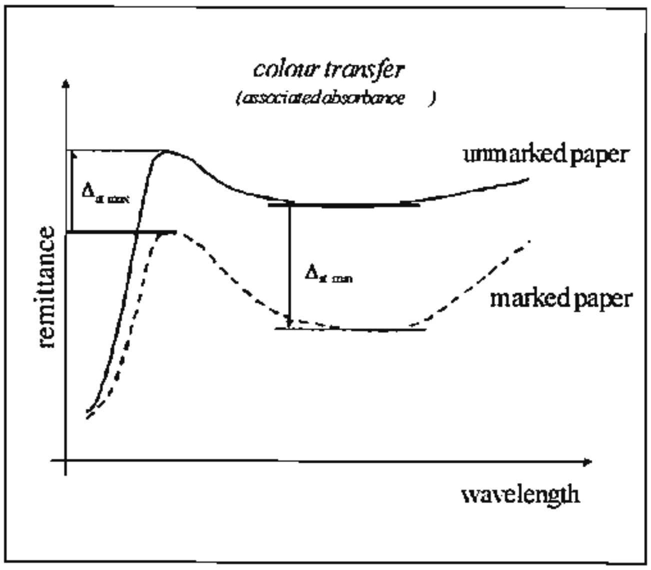


Figure 3 Schematic of the spectral remittance difference methods that can be used to describe the print rub ink transfer.

A second unprinted strip of the same paper sample is attached with double-sided adhesive tape to the metal rub off roller. The metal disk is mounted on the ISIT device (in the place of the normal printing wheel), and the brake attached. The sample carrier is rotated for the chosen number of nip passes (again in our case at a speed of 0.5 ms$^{-1}$), such that the printed strip is brought into contact with the unprinted surface under conditions of applied normal pressure (applied force across the 2 cm wide disk = 500 N) and the braking torque. The strips rotate together while the brake causes a stress in the printed ink layer via the applied torque of 0.25 Nm. The rub off effect becomes visible on the unprinted strip, *Figure 4*.

After the test, both strips are removed from the test device, *Figure 5*. The spectral remittance is measured as described above and reported as remittance as a function of illuminated wavelength.

Normally a measurement series of 10 printed strips is made with varying numbers of revolutions [0, 3, 5, 8, 10, 12, 14, 16, 18, 20, 50]. This allows, if necessary, for scaling the degree of rub off more accurately to cover a range from severe to slight rub off as a function of rotation number and spectral remittance.

### Pre-rubbing

To investigate the impact of deforming the sheet, to reflect the response under the contact pressure and shear expected to induce print rub, a method of pre-rubbing was devised. The technique follows that of the rub test described in the previous section, but with the use of an unprinted sheet in place of the usual printed sheet in contact with the contra- or contact sheet. This pre-rubbed unprinted sheet, parts of which are submitted to surface and pore analysis, under scanning electron microscopy (SEM) and confocal laser microscopy (CLSM), to determine the surface roughness profile changes, and mercury porosimetry, respectively, provides the surface for subsequent printing and undergoes finally the print rub test procedure. In this way, comparison can be made between the resistance of the paper to print rub before and after progressive compression and deformation under the shear conditions of the print rub method.

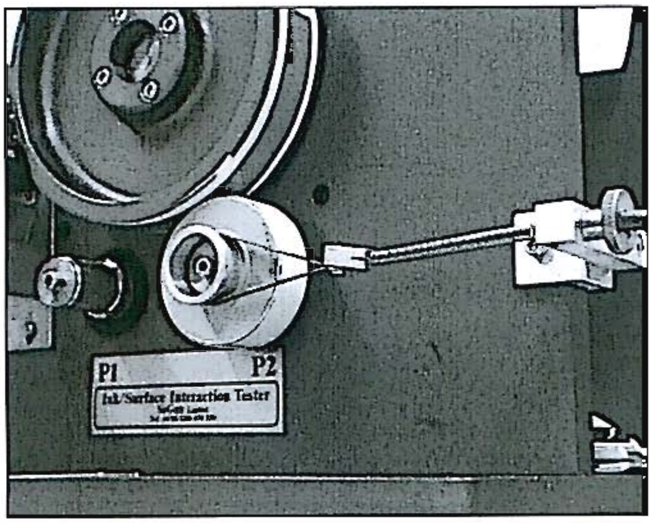


Figure 4 The test in action as the printed sheet is contacted with the unprinted sheet under pressure and braking strain.

## Results I - the impact of pore size and conformability of double coated papers

### Pre-rubbing

Four commercial matt double coated papers, A, B, C and D, were run through the pre-rub test (without printing) and the microscopic surfaces viewed by SEM images before and after the test to see the "rub" markings induced by bringing the papers together under friction. Two of the papers, labelled A, MF 135 nCC-60 (where MF refers to machine finished 135 gm$^{-2}$ paper and CC-60 is a narrow particle size gcc having 60 wt% < 1 $\mu$m applied in the pre and topcoat) and B, MF 135 bCC-75/Finegloss (where bCC is a broad particle size gcc containing 75 wt% < 2 $\mu$m and Finegloss contains 80 parts by weight of fine gcc (95 wt% < 2 $\mu$m) and 20 parts by weight of fine US glossing clay in the topcoat applied to the same precoat as on paper A), have the coatings applied to the same basepaper, and two further papers, C being a commercial matt grade containing satin white and D, a commercial semi-matt grade, adopt completely different coating-basepaper combinations. The papers were measured after 5, 15 and 50 pre-rub passes.

The SEM images before the test and at 50 pre-rub passes are shown on next page, *Figures 6-9*. The images are shown at 2 500x magnification. In each case the two pictures represent a) 0 and b) 50 pre-rub passes.

Papers A and B showed areas of strong compression after as little as 5 passes. Paper C showed areas of compression after 15 passes, and paper D showed areas of compression only after a large number of passes (50).

Paper surface roughness profiles after pre-rubbing were determined using CLSM. The grey-scale (or colour) of a CLSM-image is a function of height and enables a 3D view of the surface to be produced. Using an image analysing programme it is possible to calculate the mean and the standard deviation of the height values about an average plane. The derived parameter for expressing roughness is the standard deviation of the profile about the mean plane. Four CLSM images were taken of each paper at two magnifications, 200x and 1 350x, after 0, 5, 15 and 50 pre-rub passes.

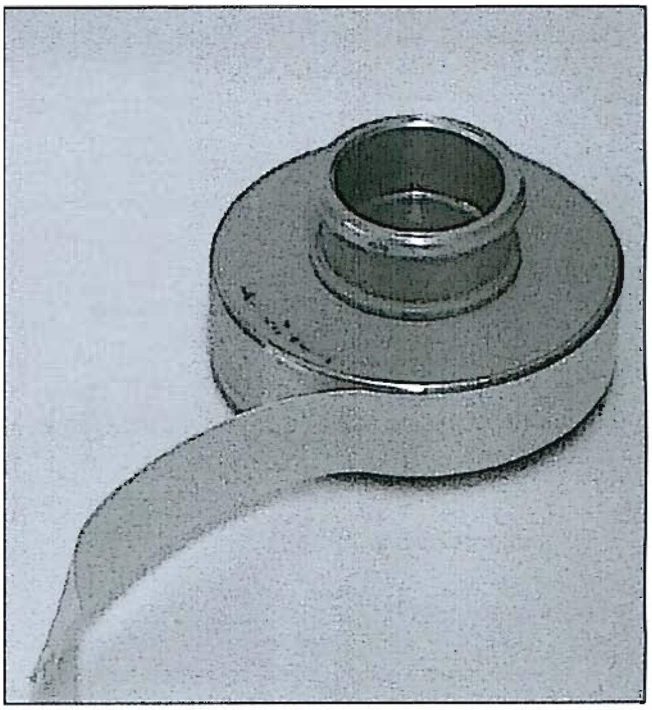


Figure 5 Removing the contact strip for spectral analysis.

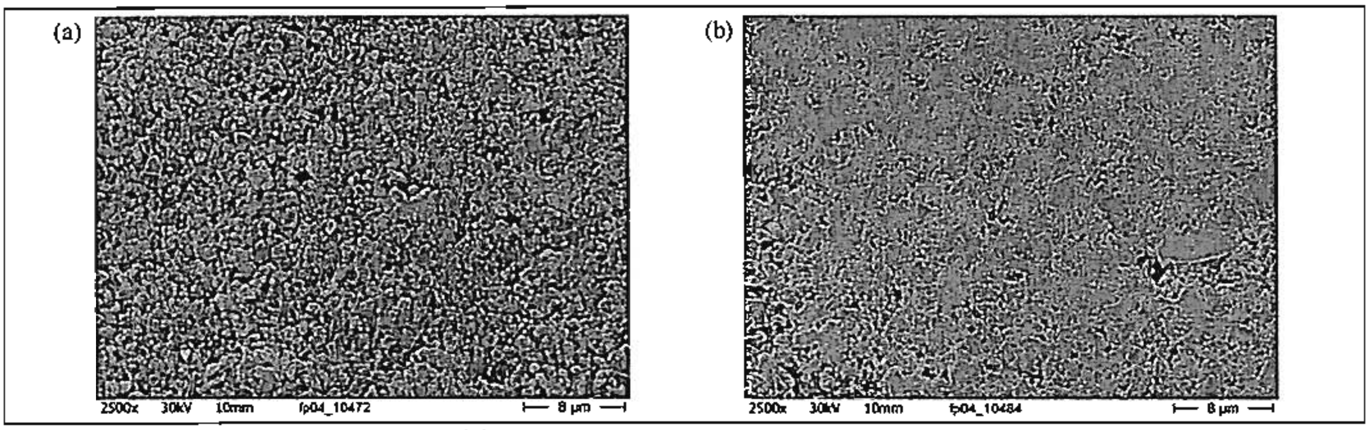


Figure 6 Paper A: MF 135 nCC-60, without pre-rubbing and after 50 pre-rub passes, respectively.

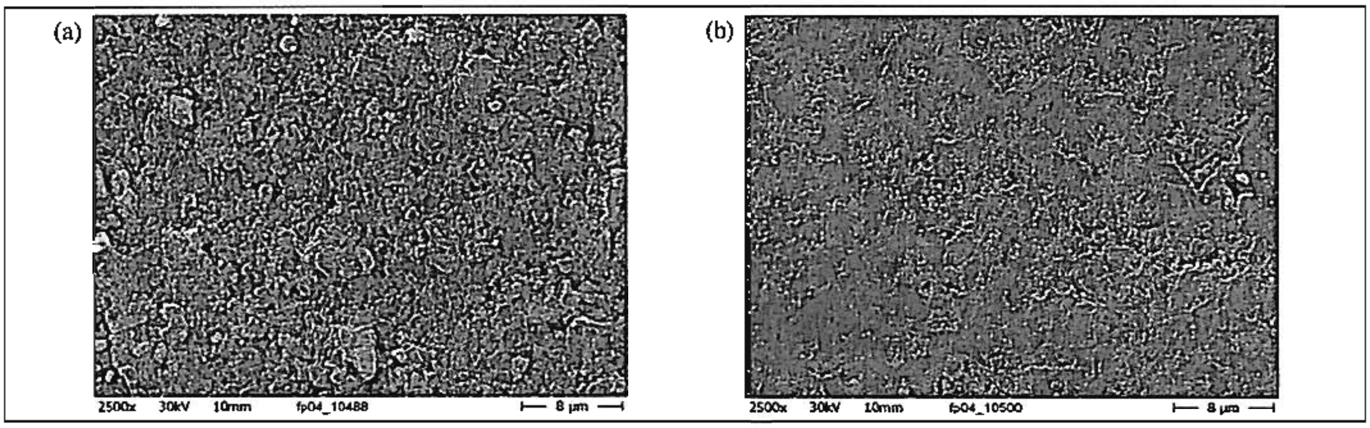


Figure 7 Paper B: MF 135 bCC-75/Finegloss, without pre-rubbing and after 50 pre-rub passes, respectively.

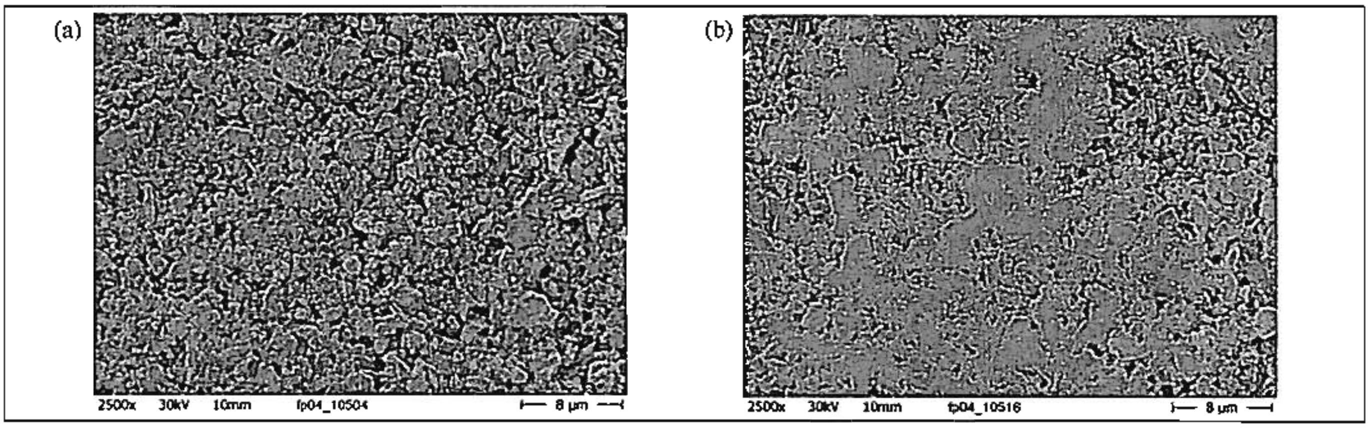


Fig. 8 Paper C: matt, without pre-rubbing and after 50 pre-rub passes, respectively.

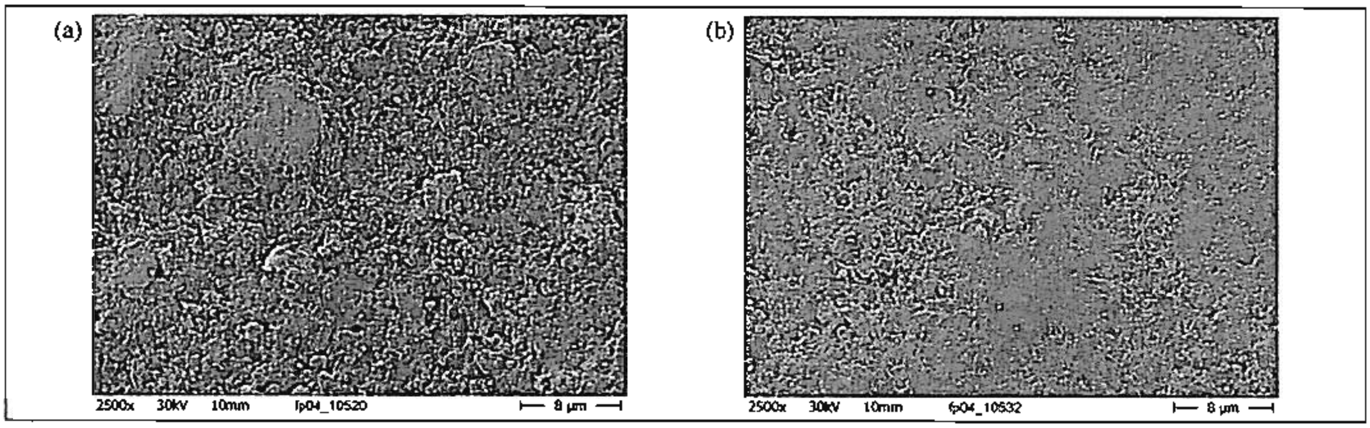


Fig. 9 Paper D: semi-matt, without pre-rubbing and after 50 pre-rub passes, respectively.

An example of a surface image is shown in *Figure 10* for Paper C before any pre-rubbing. The standard deviations for all the images taken were calculated and the average of the four values for each paper, magnification and number of pre-rub passes are plotted in *Figure 11 and Figure 12*.

All the papers have a similar average roughness, but papers A and B are considerably more uniform than papers C and D. For the two papers A and B no further smoothening effect is seen or not retained after pre-rubbing to any great extent - this may be due either to the elasticity of the papers or the lack of any conformability at all. The papers C and D, on the other hand, are smoothed to a state of being considerably more uniform by this pre-rubbing operation, *Figure 12*, indicating a higher degree of conformability under compression and shear.

The internal pore-related structural changes of the papers were measured using mercury porosimetry. When using the mercury porosimetry technique to measure papers there are often irreproducible differences between the samples at equivalent Laplace diameters greater than 10 $\mu$m, which are generally

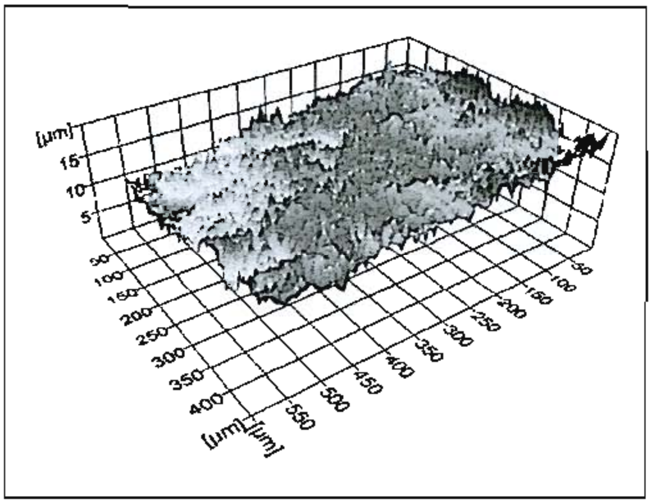


Figure 10 Example of a CLSM profile plot of paper C before pre-rubbing at 200x magnification.

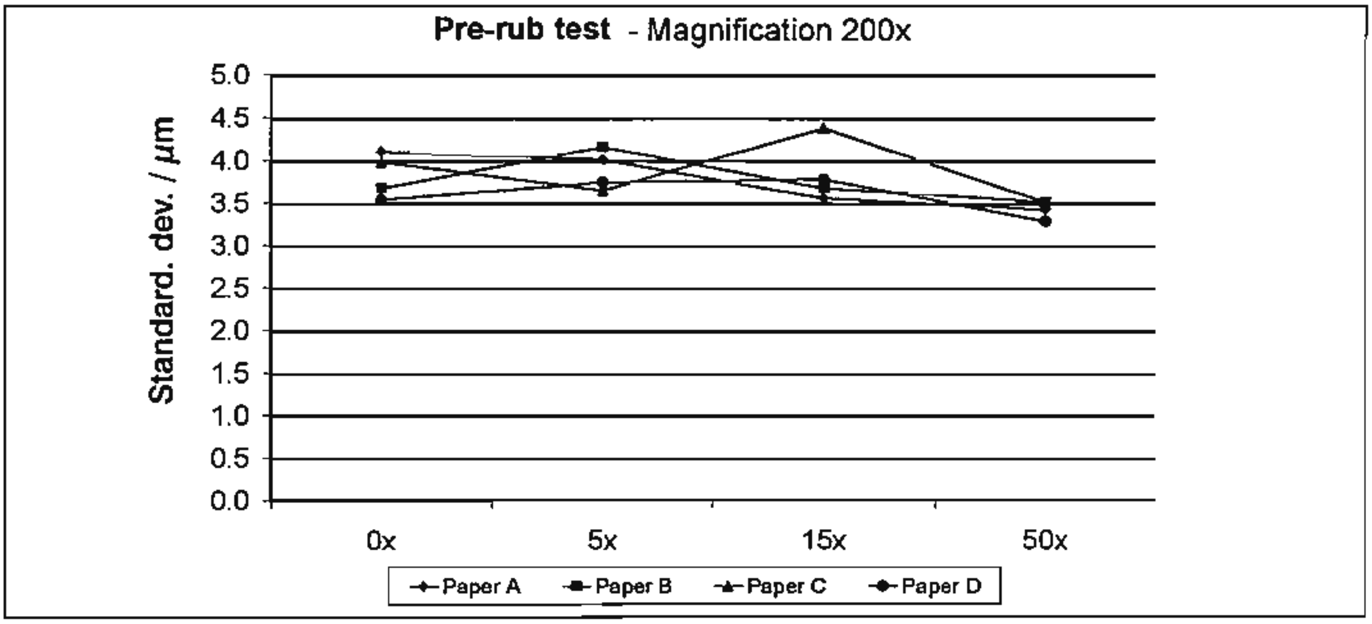


Fig. 11 Standard deviation of roughness by CLSM at 200x magnification for papers A, B, C and D.

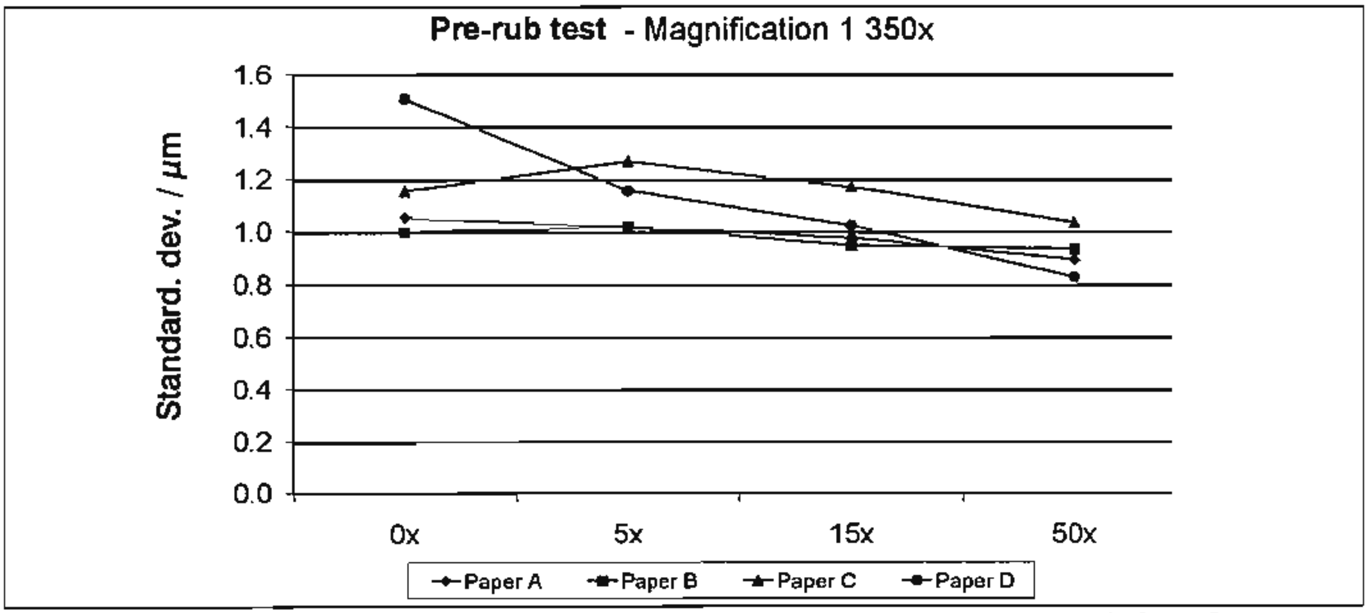


Fig. 12 Standard deviation of roughness by CLSM at 1 350x magnification for papers A, B, C and D.

attributable to the occlusion effect due to the irregularity of surface fibres, as described by Ridgway and Gane[27]. The data have therefore been truncated at a Laplace-derived pore size of 10 $\mu$m. The resulting curves are shown in *Figure 13*.

The intrusion curves for the papers, as for most coated samples, are bimodal, the larger voids represent the paper structure and the finer pores represent the paper coating structure. It is clear from *Figure 14* that paper C has the least overall pore volume change after rubbing, despite the observed conformability toward uniformity shown from the surface roughness analysis, suggesting that the basepaper has the dominant roll to play during rubbing and that the outlying high and low points of the paper are statistically reduced in the compression. This paper also has the lowest total pore volume.

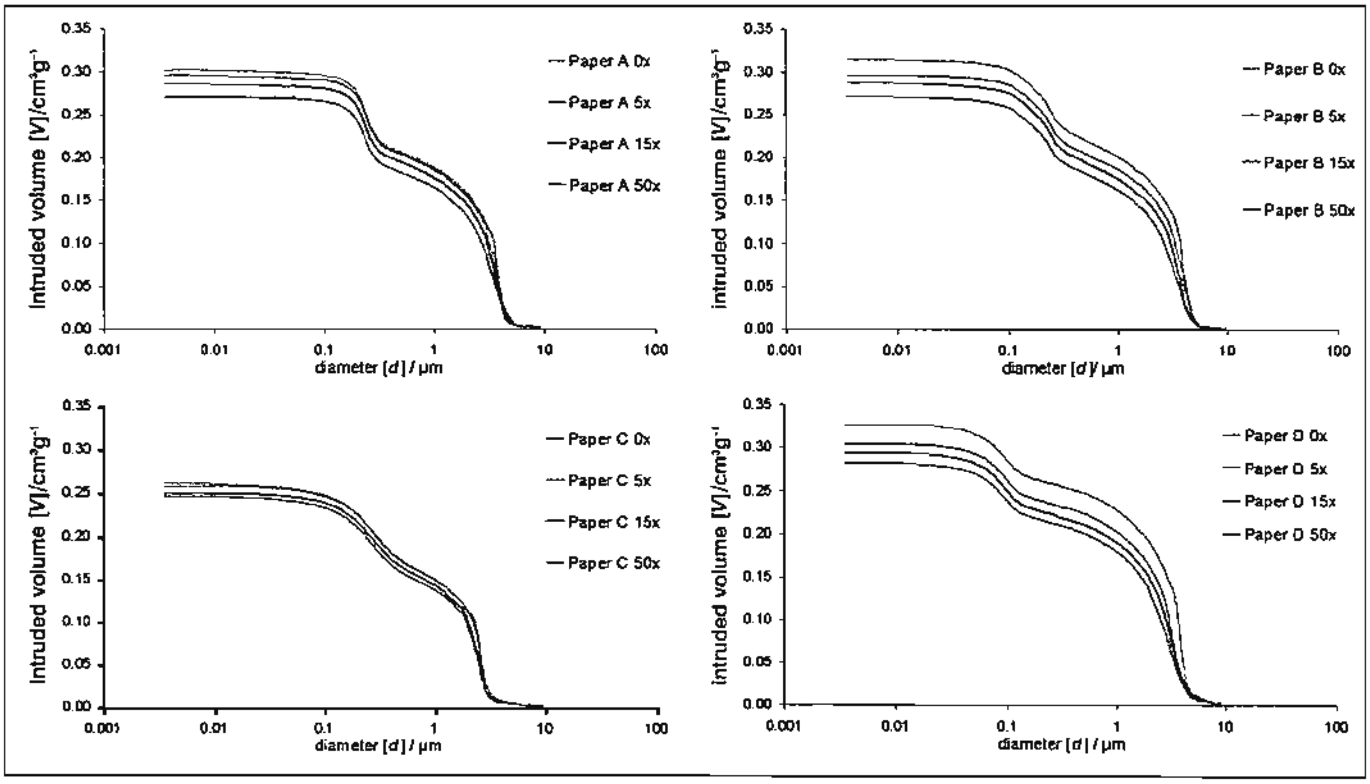


Figure 13 Mercury intrusion curves for papers A, B, C and D before and after progressive pre-rubbing.

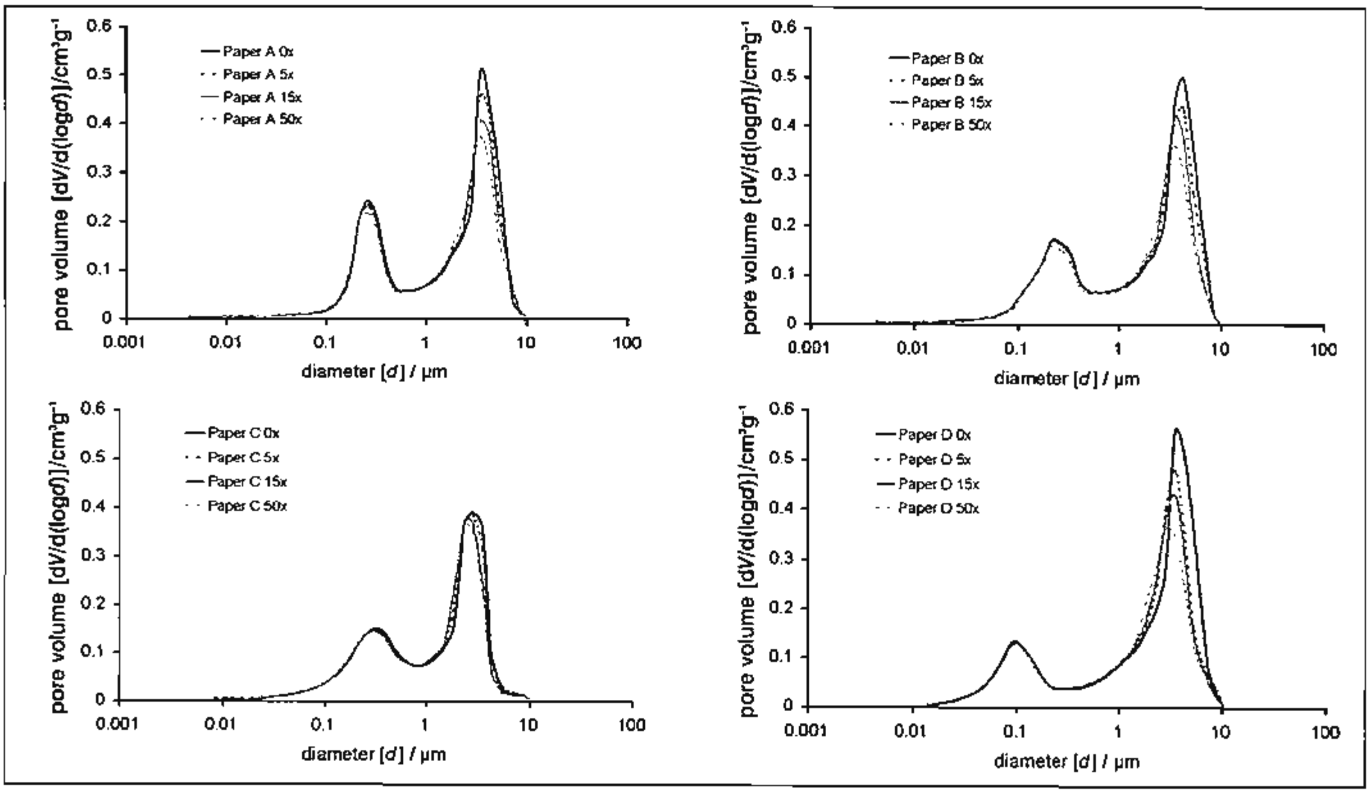


Figure 14 Differential mercury intrusion curves for papers A, B, C and D before and after progressive pre-rubbing.

The coating structure of Paper A, containing the narrow particle size nCC-60, is shown to be less compressible than that of paper B containing the Finegloss pigment mix of broad size distribution fine gcc and US glossing clay. Given that the basepaper is the same in these experiments, and described above as incompressible, any differences in end performance after pre-rubbing will derive, therefore, from the coating differences alone.

By taking the first derivative of the cumulative intrusion curves, the pore size distributions based on equivalent Laplace diameter, inevitably including pore-shielding effects, are revealed. These are shown in *Figure 14*.

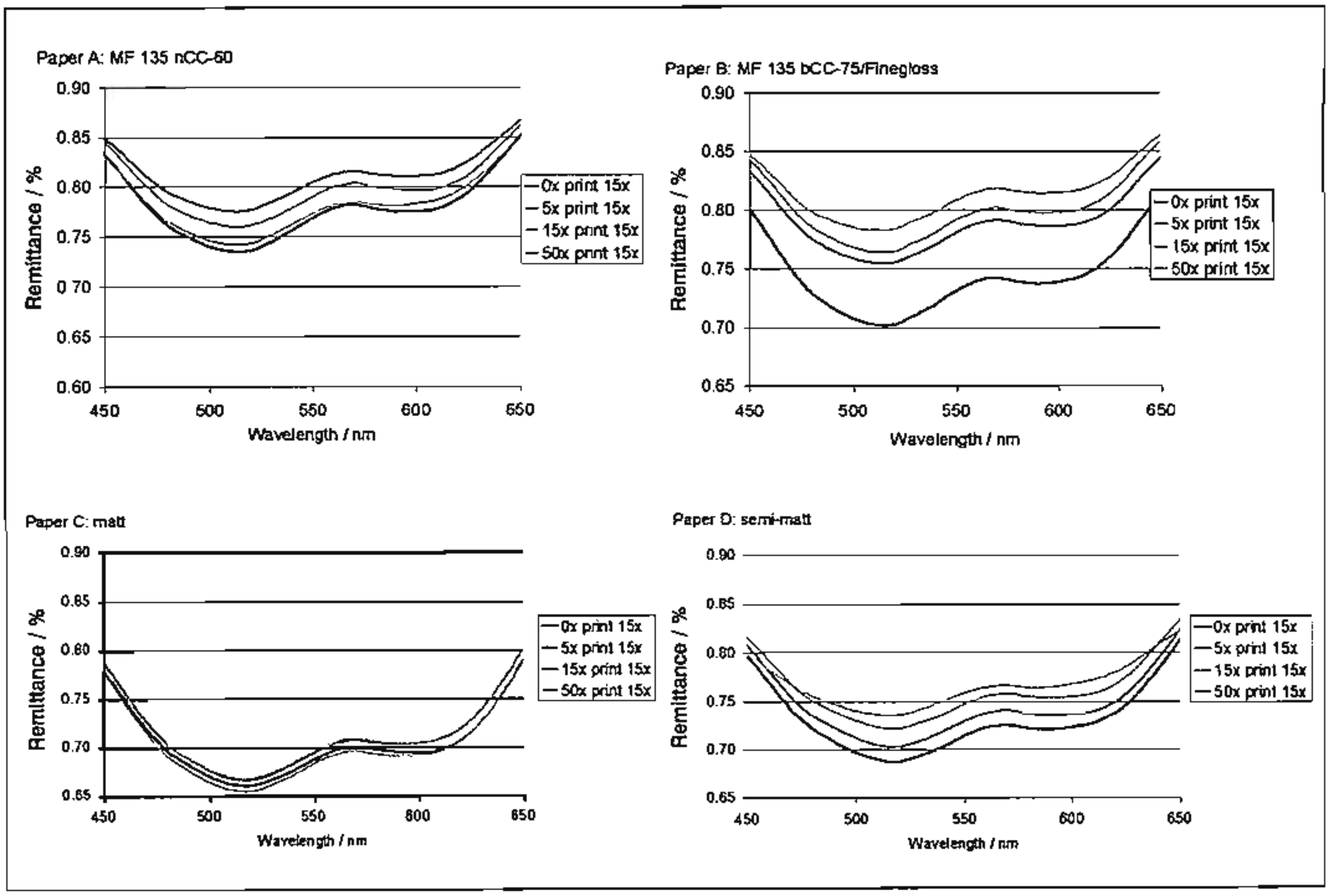
These diagrams show that there is very little change in the coating pore volume for paper C and paper D after pre-rubbing. Paper D basepaper, however, (the larger peak) is shown to reduce in pore size with increased pre-rubbing, also confirming the surface analysis suggesting conformability of this structure. Paper C, however, also has the smallest total pore volume reduction when compared to all the other papers and the basepaper peak in this pore size range is shown to be the most stable. Compression therefore is related to large pore sizes in the basepaper not recorded here. The coating pore volume is reduced for both papers A and B under the pre-rubbing process. The coating peak for paper A is not as broad as those for the other papers, reflecting the narrow particle size distribution of the pigment used nCC-60, resulting in a narrow pore size distribution.

**Pre-rubbing, Printing and Post- rubbing**

*Figure 15* shows the remittance values from the photospectroscopy measurement from the respective unprinted contact sheets. In the legend the first number is the number of pre-rub passes. The samples, each with their various pre-rub conditions, were then printed, left for 72 hours and then rubbed again with 15 passes, as defined by the second number in the legend.

The results from paper A show an inverse trend in comparison to the other samples, i.e. the print rub of the paper improves after slight pre-rubbing but then deteriorates again strongly after further pre-rubbing. This paper with its narrow particle size distribution in the coating fails to generate finer pores under compression, as was seen from the porosimetry in *Figure 14*. Pre-compressing the paper at first does make some small number of finer pores together with a slight amount of smoothing. However, further pre-rubbing only increases detrimentally the contact area for rub to take place on an otherwise mono-pore size surface. This paper, therefore, develops a high surface contact area, which is seen to increase after just 5 passes during the pre-rubbing trial, and any significant pre-rubbing (representing calendering perhaps) is seen to make print rub worse.

The other samples, B, C and D contain fine pores in the coating, either from the formulation or as a result of the pre-rubbing or both. Therefore, the greater smoothness, if present, after pre-rubbing, which created the negative effect on paper A of increased contact, is over-ridden by the benefits the finer pores give to the ink setting and rub resistance of the ink.


Paper A: MF 135 nCC-60

Paper B: MF 135 bCC-75/Finegloss

Paper C: matt

Paper D: semi-matt

Figure 15 Remittance values of print rub contact sheet using the "standard" stay-open ink: tested after progressive pre-rubbing followed by printing and print rub testing at 15 passes.

For completeness, the remittance values are compared between the print rub transfer sample and the original pre-rubbed paper, i.e. the remittance difference between the background pre-rubbed paper and the transferred print rub sample of ink onto fresh paper undergoing the defined number of 15 print contact rubs. This allows the papers to be directly compared. *Figure 16* shows the rub off test comparison from the pre-rubbed unprinted papers (pre-rub passes 0, 5, 15 and 50) with the transfer density after 15 passes. The graphs compare the 4 paper types, where the spectra are defined as {Remittance of background paper - Remittance of print rub contact paper}.

We see from these graphs, that, when the background Remittance of the underlying sheet is considered, the matt paper C is actually not good for print rub in terms of contrast of transferred ink density. The tendency for paper A to be generally reported in practice as being poor is shown to be confirmed, i.e. initial improvement after slight pre-rubbing, but deterioration after heavy pre-rubbing (which could be interpreted in practice, for example, as calendering) in comparison with the other 3 papers.

**Interim Finding I**

From this first series of analyses, we extract the first indications of the interactive role-play of basepaper and coating structure in determining the level of rub resistance that can be expected from a matt or silk paper. Confirmation is now needed to see how the factors of coating and basepaper cross-correlate, i.e. a fine pore coating that is compressible is expected to compensate for small roughness variations in the basepaper. Conversely, a large pore coating that is itself incompressible copes poorly with basepaper incompressibility and roughness. In order to do this it is required that a series of samples be chosen that illustrate extremes of roughness and conformability response, such that the differences in coating structure and basepaper structure can be investigated.

## Results II - effect of basepaper conformability

Using the pre-rub test, some papers displayed high 'stretchability'. This has a negative impact in the test if measures are not taken to avoid it. Two coated papers, E and F, in the form of matt and semi-matt finishes on the same basepaper, showed some stretchability under this test. These two papers were then investigated for their print rub properties and compared with a non stretching paper, G. *Figure 17 (overleaf)* shows the degree to which a paper, after passing through the braked nip, i.e. under shear, exhibits elongation and wrinkling at the trailing end if the paper is also attached here to the rotating sector of the ISIT.

For the subsequent work using stretchable papers, the paper strips were only attached by the leading edge, allowing the paper to stretch in the direction of shear as necessary without creasing.

**Pre-rubbing**

The papers E and F (135 gm$^{-2}$) and the paper G were run through the rub test without printing and the surfaces viewed by SEM before and after the test to see the "rub" markings induced by bringing the papers together under friction after 0, 5, 15 and 50 passes, as was performed in Part I of this work. The SEM images before the test and at 50 passes, at 2 500x magnification, are shown below, *Figures 18-20 (overleaf)*.

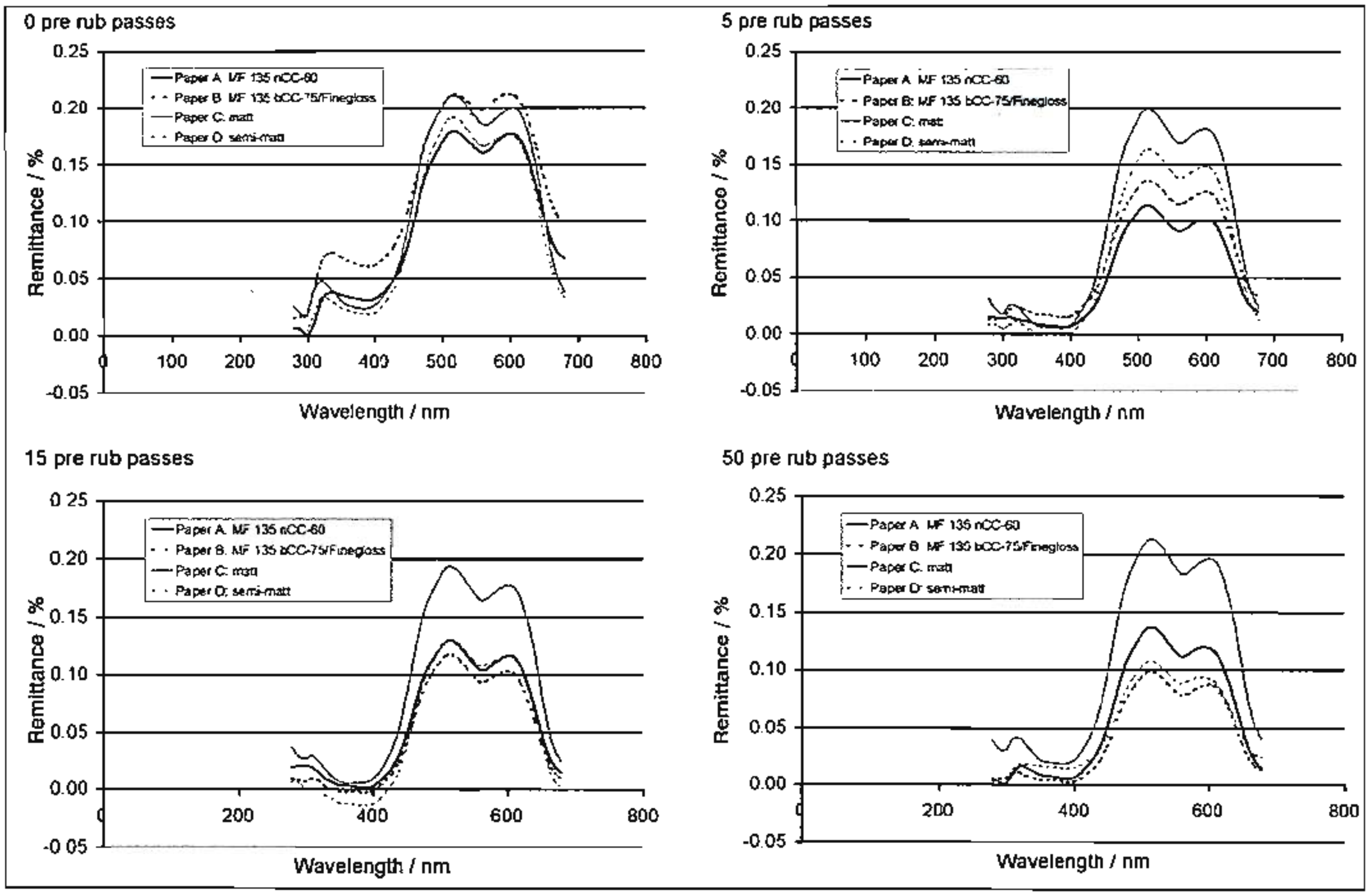


Figure 16 Remittance difference values for papers A, B, C and D using stay open ink in a 15 pass print rub test following progressive pre-rubbing.

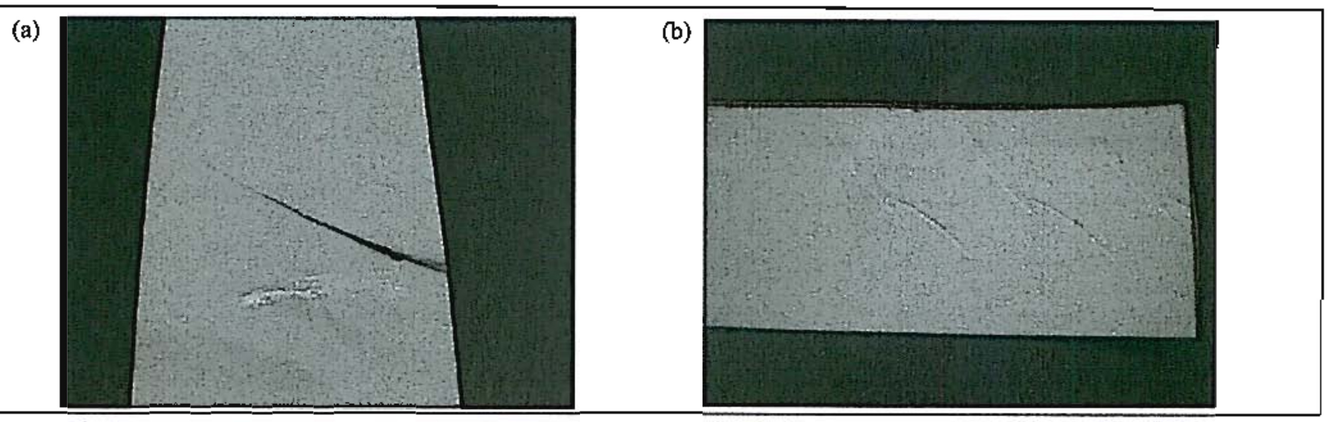


Figure 17 Stretching and crinkling of paper E after pre-rubbing with 50 passes when both ends are held. a) Pre-rubbed strip showing wrinkling/creasing due to stretch under shear - note the glossing effect - this in turn damages the contact rub strip b).

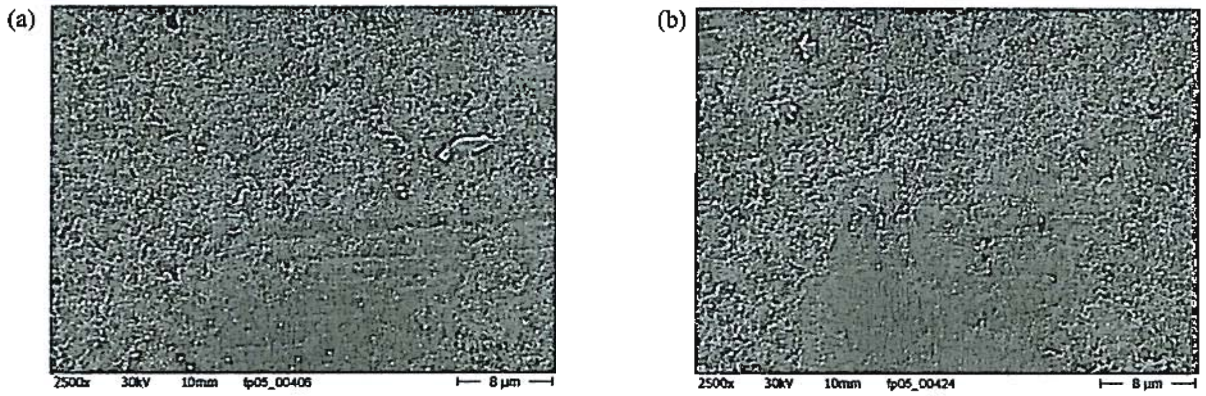


Figure 18 Paper E - stretchable matt, before and after pre-rubbing at 50 passes.

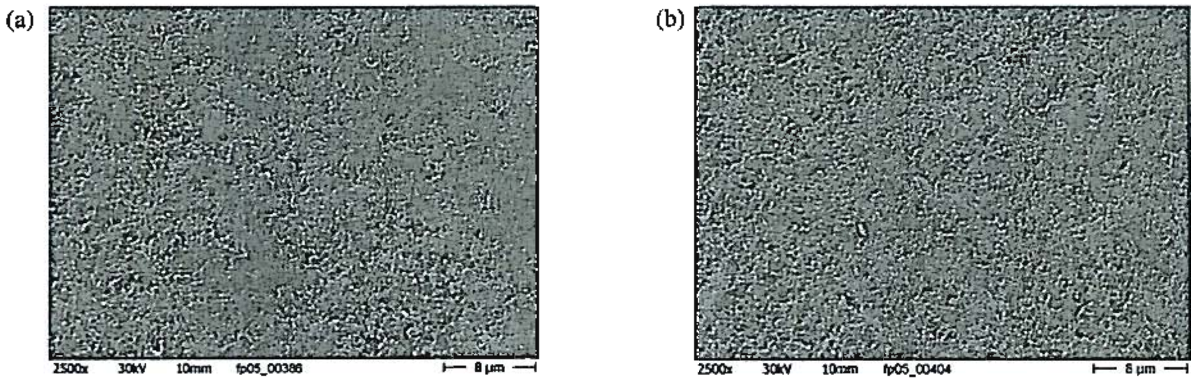


Figure 19 Paper F - stretchable semi-matt, before and after pre-rubbing at 50 passes.

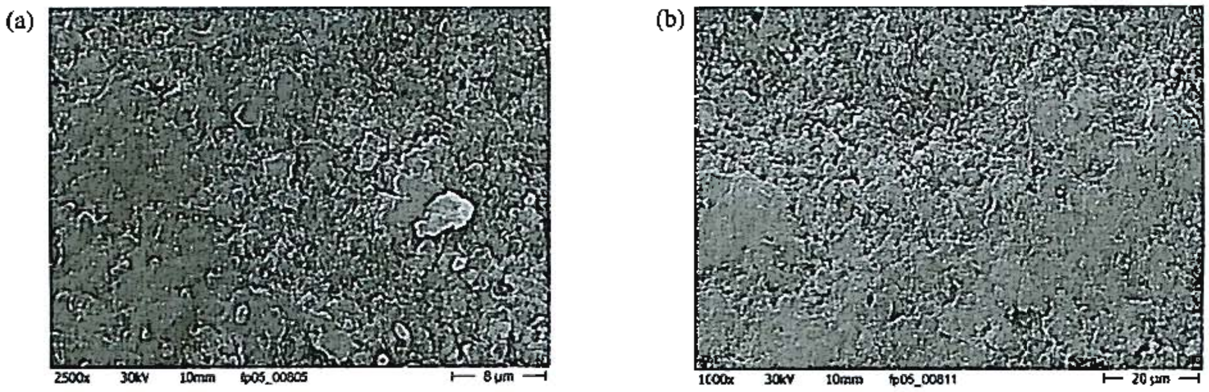


Figure 20 Paper G - non-stretchable matt, before and after pre-rubbing at 50 passes.

Papers E and F matt and semi matt show the use of a much finer pigment formulation than in the case of paper G. All three papers, however, show areas of strong compression after as little as 5 passes, the least affected being paper F, the semi matt paper, which is likely to have had some finishing/calendering to create the higher gloss (less mattness). Paper G despite having a coarser coating structure still shows very strong areas of compression reducing the originally coarse coating structure to one of almost complete closure (or many fine pores) at the points of contact. It is expected that such a paper would show strong gloss marking.

Paper surface roughness after pre-rubbing, as in the previous section, was analysed using CLSM, again at two magnifications, 200x and 1 350x, after 0, 5, 15 and 50 passes through the frictional ISIT print rub mounting, and the standard deviations of the roughness profiles were calculated incorporating a correction for the shading caused by the undulating paper surface which arises as the paper stretchability or elasticity increases. The average of the four values for each paper type, magnification and number of passes are plotted in *Figures 21 and 22.*

At a magnification of 200x the stretchable matt and semi matt papers, E and F, respectively, appear to become rougher with increased pre-rubbing, whereas the rigid paper G sample has a smoother surface with increased pre-rubbing. This roughening effect is assumed to be related to the stretchability of the samples and is reflected in the large-scale roughness only. When looking at the papers at 1 350x magnification the papers show little change with increased pre-rubbing. Paper G has a greater fine-scale roughness than the matt and semi matt papers, E and F, relating mostly to the differences in coating pigment structure.

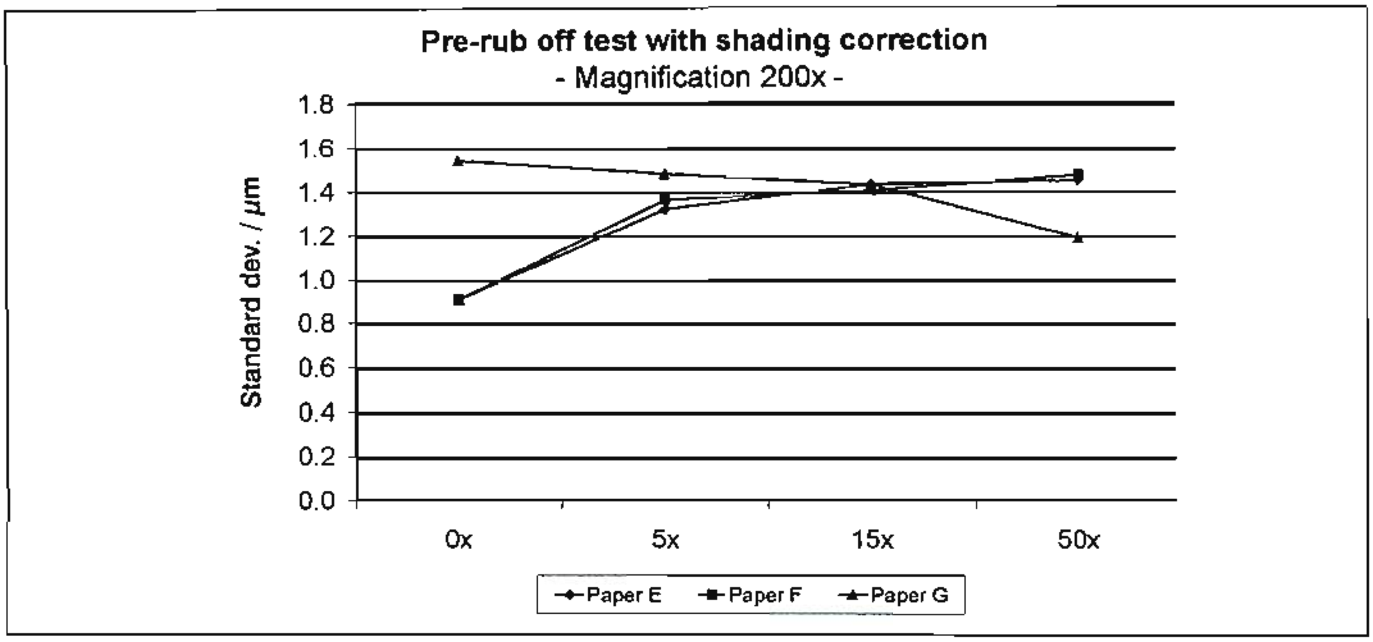


Fig. 21 Standard deviation of roughness by CLSM at 200x magnification for papers E, F and G - note the roughness increase of the deformable papers E and F.

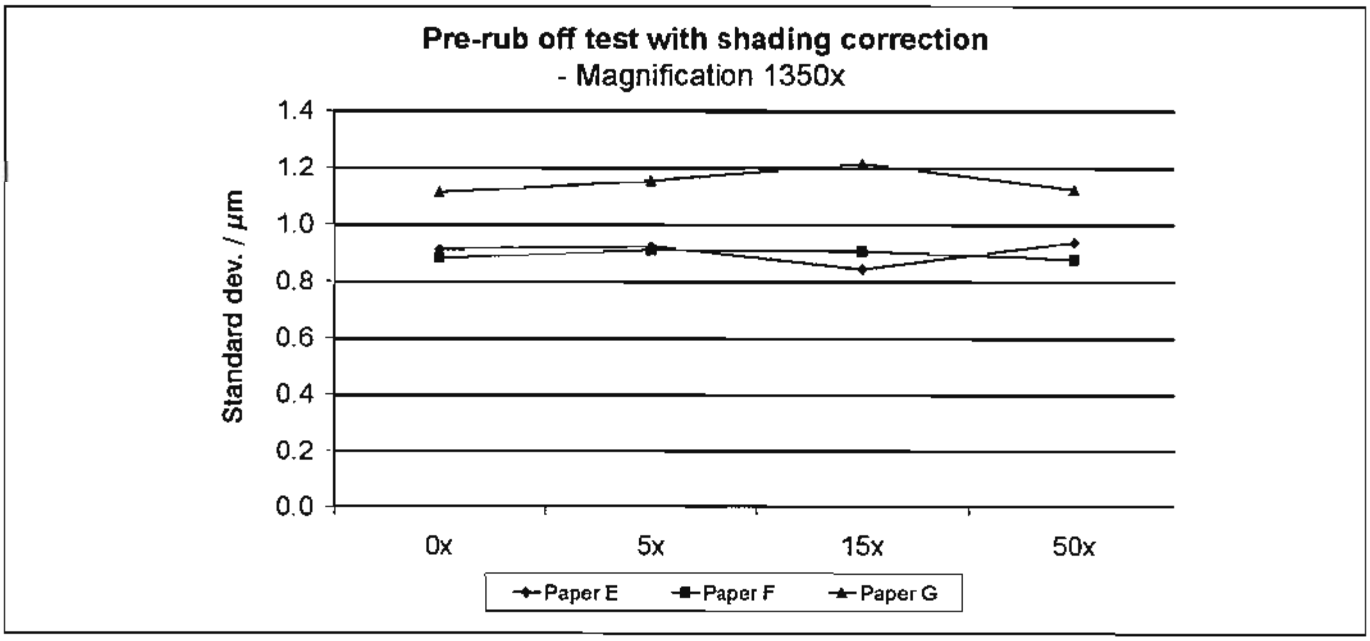


Fig. 22 Standard deviation of roughness by CLSM at 1 350x magnification for papers E, F and G

The internal structural changes of the papers were measured using mercury porosimetry. The intrusion curves for the papers, as for the previous samples, are bimodal, the larger voids represent the finer basepaper structure and the finest pores represent the paper coating structure. It is clear from *Figure 23* that the semi matt paper F has the least pore volume change after pre-rubbing. This paper also has the lowest total pore volume.

The equivalent Laplace diameters, inevitably including pore-shielding, are shown in *Figure 24*.

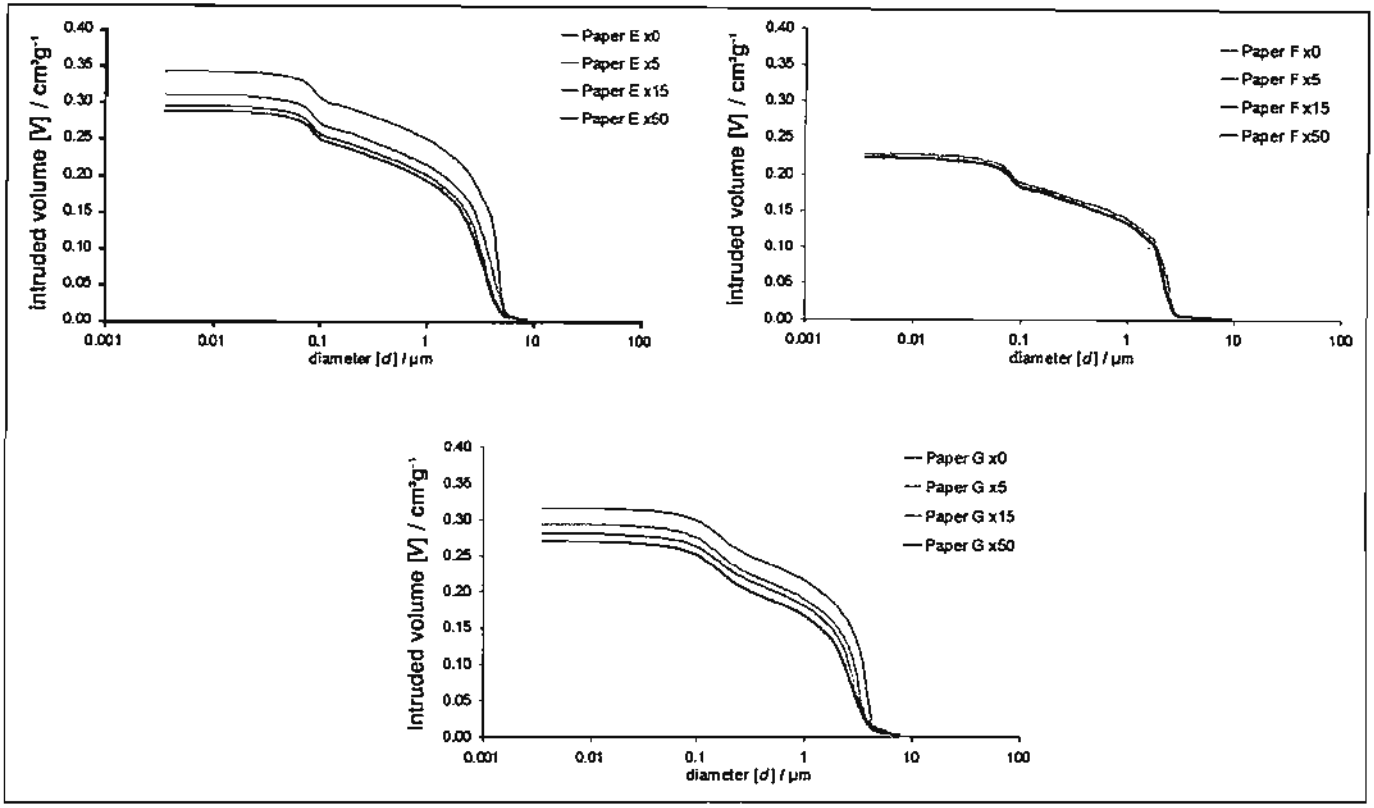


Figure 23 Mercury intrusion curves for the papers E, F and G as a function of progressive pre-rubbing.

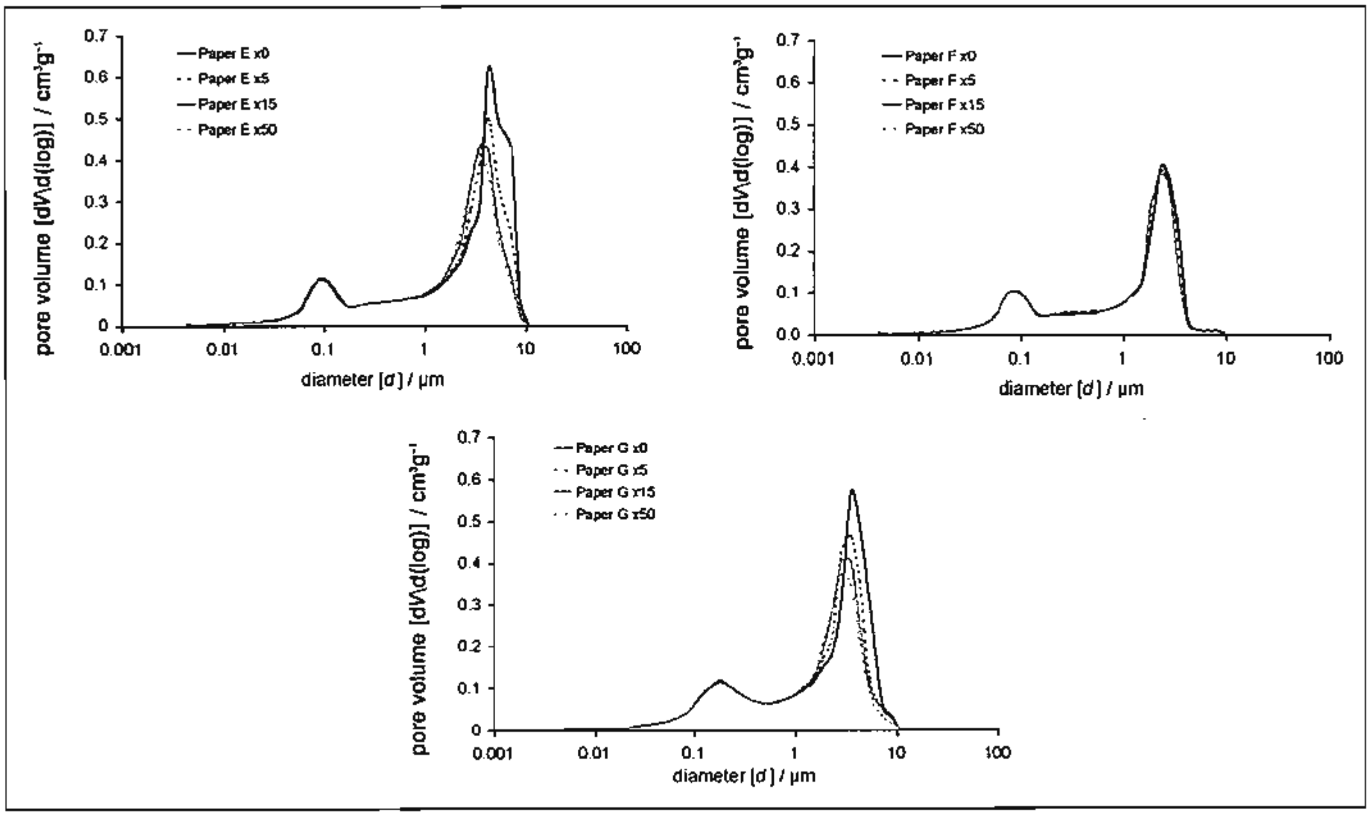


Figure 24 Differential mercury intrusion curves for papers E, F and G, showing the pore volume distributions as a function of Laplace pore diameter before and after progressive pre-rubbing.

These data show that there is very little change in the coating volume for all the paper samples after pre-rubbing. The coating peak for paper G is slightly broader than those for the other papers, reaching into the larger coating pore region, which can be seen also in the previous SEM images, *Figure 20*. The basepaper for the semi matt paper F is the most stable, suggesting a likely finishing/calendering step in production such that there is little volume change after pre-rubbing. The matt paper E and non-stretchable paper G do show a reduction in volume and pore size with pre-rubbing.

**Pre-rubbing, Printing and Post-rubbing**

*Figure 25* shows the remittance values from the photospectroscopy measurement from the unprinted contact sheet. In the legend, the first number is the number of pre-rub passes. The pre-rubbed samples were then printed, left for 72 hours and then rubbed again with 15 passes, as defined by the second number in the legend.

The results from the matt sample, paper E, show that the print rub resistance deteriorates slightly after pre-rubbing at first as the roughness of the sample increases *(Figure 21)* but then recovers after 50 passes. The recovery occurs as the basepaper is further compressed resulting in a greater number of fine basepaper pores. The semi matt sample, paper F, shows an inverse trend, in that the print rub improves initially but then after 50 passes drops again. This semi matt paper is already partly compressed before any pre-rubbing has taken place. Once the pre-rubbing process is introduced there comes a point when the sample cannot be compressed any further, at this point the sample increases in roughness as the basepaper stretches. Paper G behaves in a similar manner as paper E, in that the basepaper compresses but does not stretch and so does not get rougher after pre-rubbing.

Once again, the remittance values are now compared between the print rub transfer sample and the original pre-rubbed paper, i.e. the remittance difference between the background pre-rubbed paper and the transferred print rub sample of ink onto fresh paper undergoing the number of print contact rubs. *Figure 26 (overleaf)* shows the rub off test comparison from the pre-rubbed unprinted papers (pre-rub passes 0, 5, 15 and 50) with the transfer density after 15 passes. The graphs compare the 3 paper types, where the spectra are defined as {Remittance of background paper - Remittance of print rub contact paper}.

We see from these graphs, that when the background Remittance of the underlying sheet is considered, paper G shows itself as good for print rub in terms of low contrast of transferred ink density. After 50 pre-rub passes all the papers have a similar remittance level.

## Interim finding II

Pre-rubbing increases the larger scale roughness of stretchable papers, E and F, which can be negative for print rub if the basepaper is not conformable under contact. However, stretchability and conformability probably are linked. The micro roughness, however, remains constant. We can conclude, therefore, that for paper E, where the basepaper pores became finer during compression and shear, the balance of properties is maintained and the paper is relatively insensitive to handling, returning a consistent rub resistance value. Similarly, if the paper is non-stretchable, the roughness remains controlled and pre-rubbing (finishing) acts to improve the rub resistance by

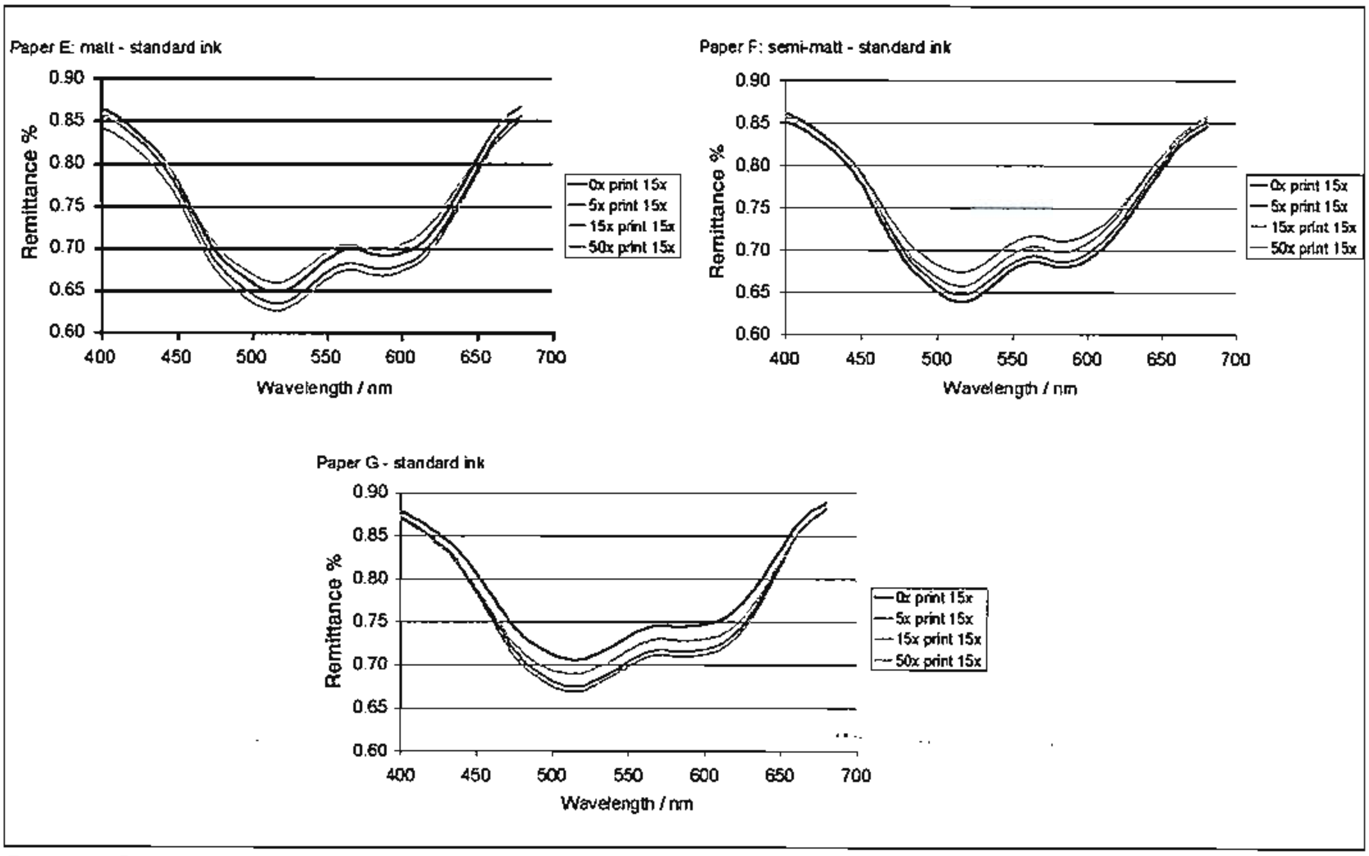


Figure 25 Remittance values of stay open ink on papers E, F and G following progressive pre-rubbing and print rub testing at 15 passes.

compressing the basepaper if it is indeed compressible, as was the case for paper G. The difference in remittance values after 50 passes shows all these papers E, F and G have a similar print rub level.

If, therefore, the roughness levels are not too great, a compressible basepaper can compensate for some roughness variation, resulting in smoothness on contact. Under conditions of fine pores being present in the coating, this leads to positive rub resistance behaviour. If, however large pores are present in the coating - low capillarity - then the converse may be true. This remaining issue is now clarified in the next series of tests in part III.

## Results III - the effect of different coating strategies

Two coated papers, H and I *(see Table 1)*, were run through the pre-rub test. In this part of the study the coating strategy is changed by comparing a single coated version, using the pigments previously discussed in part I, i.e. bCC-75 and Finegloss, and incorporating an acrylic-based latex binder, with a double coated version in which nCC-60, the narrow particle size pigment, is used as a precoat. SEM images of the surface of the papers before the test and at 50 pre-passes, at 2 500x magnification, are shown overleaf in *Figure 27 and Figure 28.*

| | | |
|---|---|---|
| Paper H | 50 parts bCC-75 and 50 parts Finegloss<br>+ Acrylic binder | single coated |
| Paper I | 50 parts bCC-75 and 50 parts Finegloss<br>+ Acrylic binder | double coated |
| Paper A | MF 135 nCC-60 | (included here as reference) |

Table 1

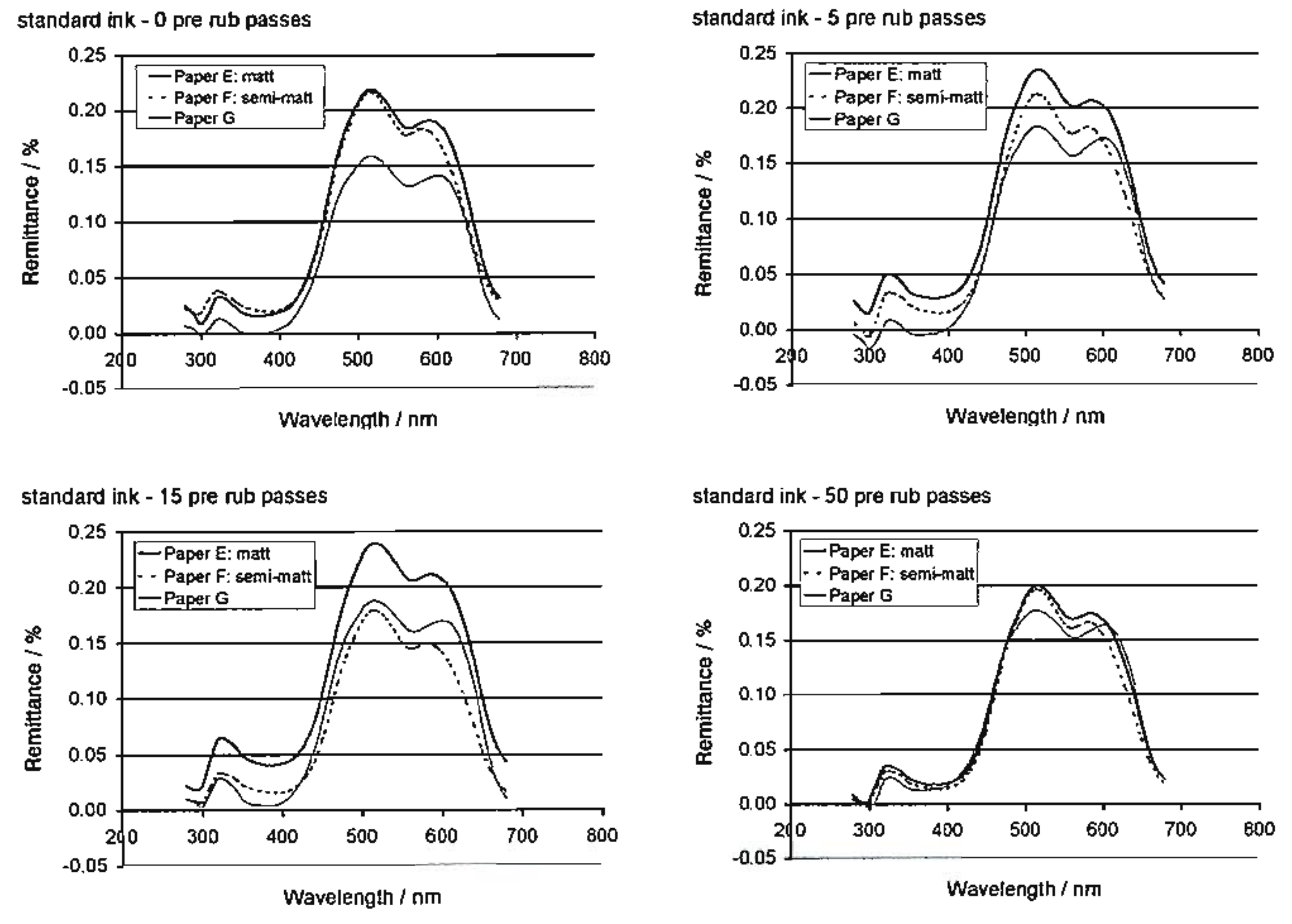


Figure 26 Remittance difference values for papers E, F and G using stay open ink in a 15 pass print rub test following progressive pre-rubbing.

*Figure 27 and Figure 28* emphasise the role of surface fibres in the single coated example. The coating above the fibre becomes compressed. In the case of the double coated example, the existence of fibre flocs in the basepaper contributes to a definite area compression effect of the coating rather than the fibre directional compression only seen in the single coating example.

Paper H, therefore, shows the fibre structure of the basepaper, as might be expected from single coated papers with less coverage or more contouring of the basepaper profile, and the coating on top of the fibres is compressed. In contrast, the double coated paper I displays a strong compression of the coating with little of the basepaper structure being visible. An initial conclusion is that the role of the basepaper is thus different between these samples. In the case of paper H the basepaper fibre compressibility is important, in case I the basepaper caliper profile is important as the precoating acts to rigidify the composite.

### Surface and Structural Analysis of Pre-rubbed / Compressed Samples

CLSM images have been used to derive the surface roughness values expressed as standard deviations and shown in *Figure 29 and Figure 30.*

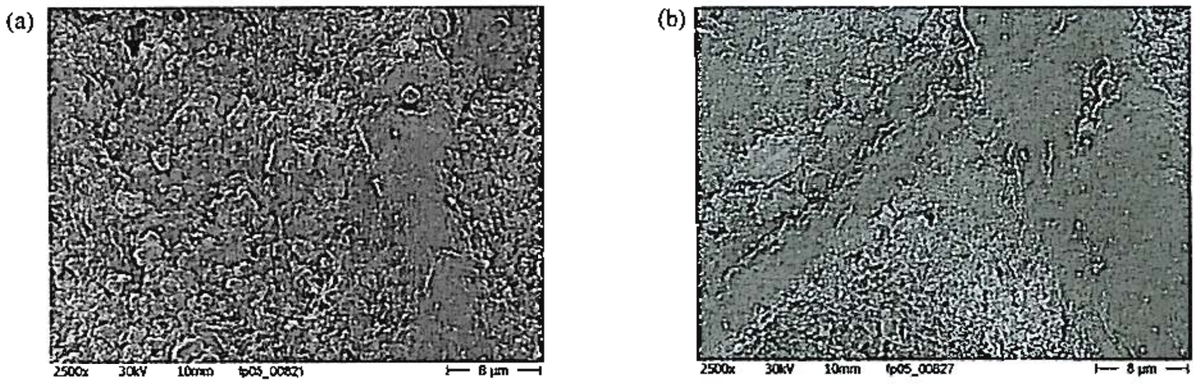


Figure 27 Paper H: single coated

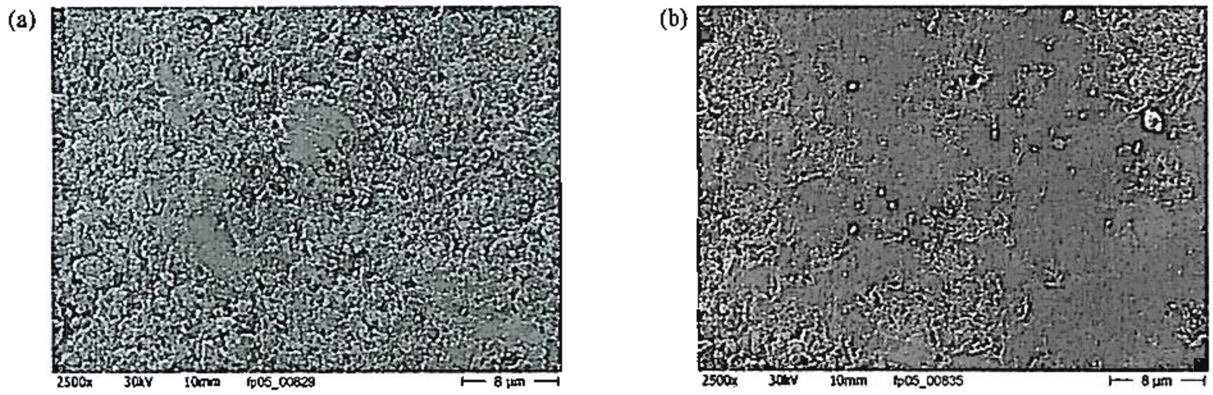


Figure 28 Paper I: double coated

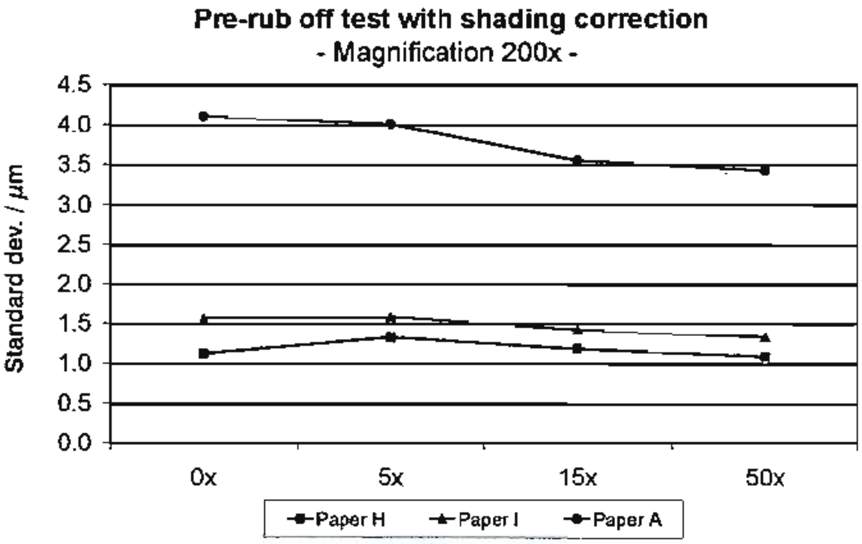


Figure 29 Standard deviation of roughness by CLSM at 200x magnification for papers H and I compared with the previously studied paper A - note how paper A is significantly rougher at this relatively coarse scale.

At 200x magnification the papers are all slightly smoothed with increasing number of passes. Paper A shows the highest roughness, but also the greatest smoothing effect. At 1 350x magnification there is a small decrease in the roughness for all papers. Paper A and paper H have the smoothest surfaces from this microscale measurement.

The mercury intrusion curves for the papers, H and I, together once again with those for paper A are shown in *Figure 31*. It is clear from these intrusion data that paper H has the most pore volume change after pre-rubbing, and Paper A the least.

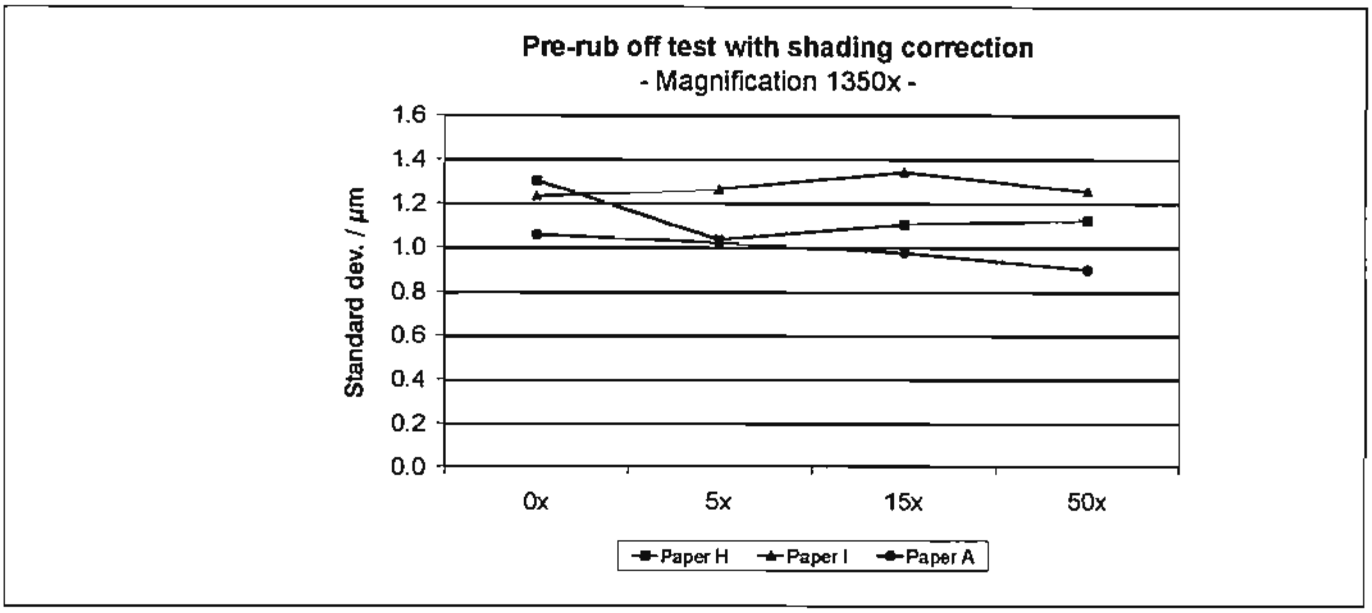


Figure 30 Standard deviation of roughness by CLSM at 1350x magnification for papers H and I. In this case paper A on the microscale is at the same smoothness level as the others.

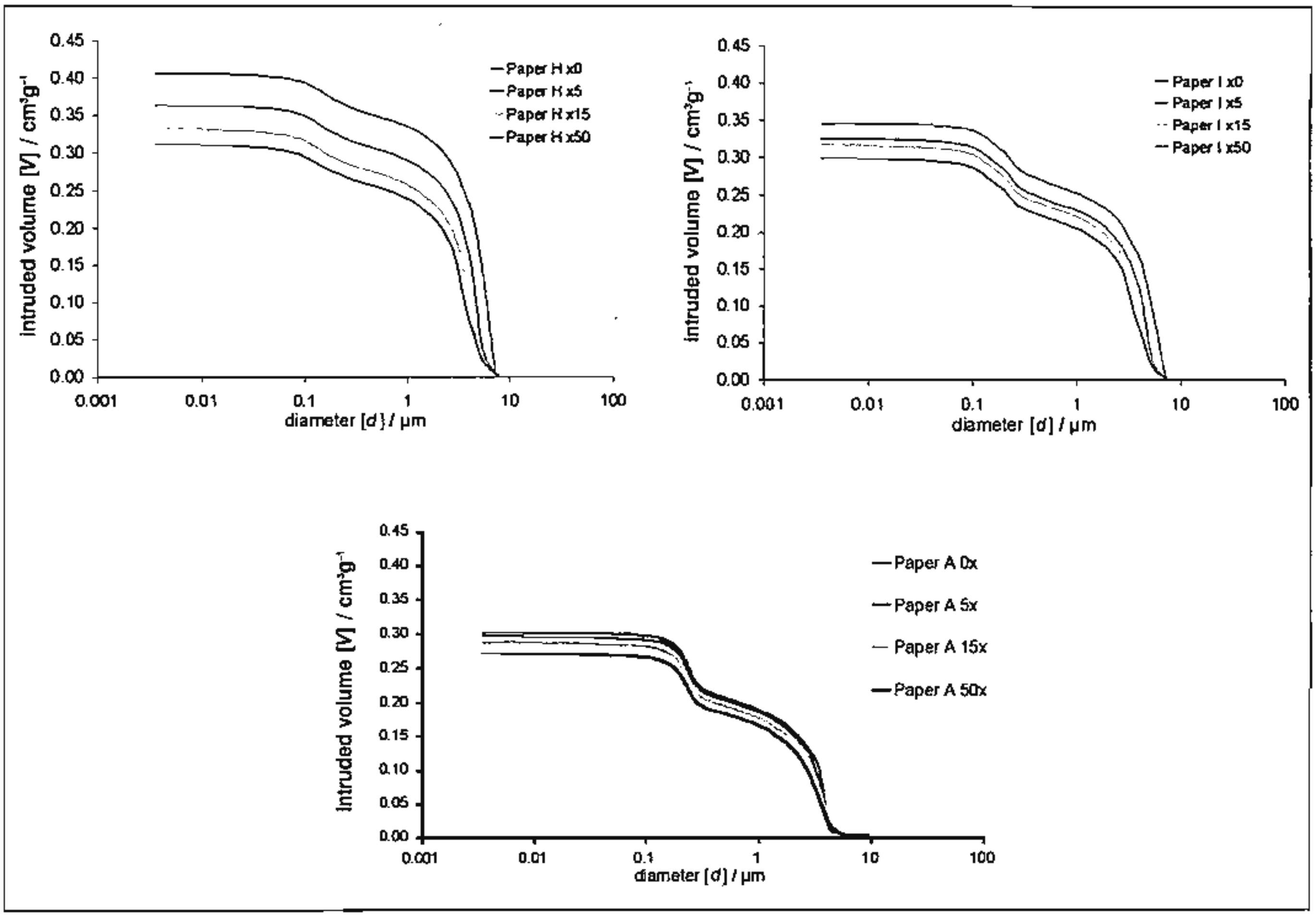


Figure 31 Mercury intrusion curves for papers H and I compared with paper A.

The equivalent Laplace diameters, inevitably including pore-shielding, are revealed in *Figure 32*.

The pore distribution diagrams show that there is a slight change in the coating volume (left hand peak) for all the samples after pre-rubbing. The coating peak for paper I is higher than those for paper H, due to this sample being double coated, and hence more pore volume is present in this region. The basepaper-coating interface peaks (right hand) for papers H and I show large changes in pore size as well as pore volume with increasing number of passes, but, once again, paper A shows the least response in basepaper change.

**Pre- rubbing, Printing and Post- rubbing**

*Figure 33* shows the spectroscopic remittance values after post-rubbing the printed samples - the legend describes the pre-rubbing passes and the print rub test made after 15 passes.

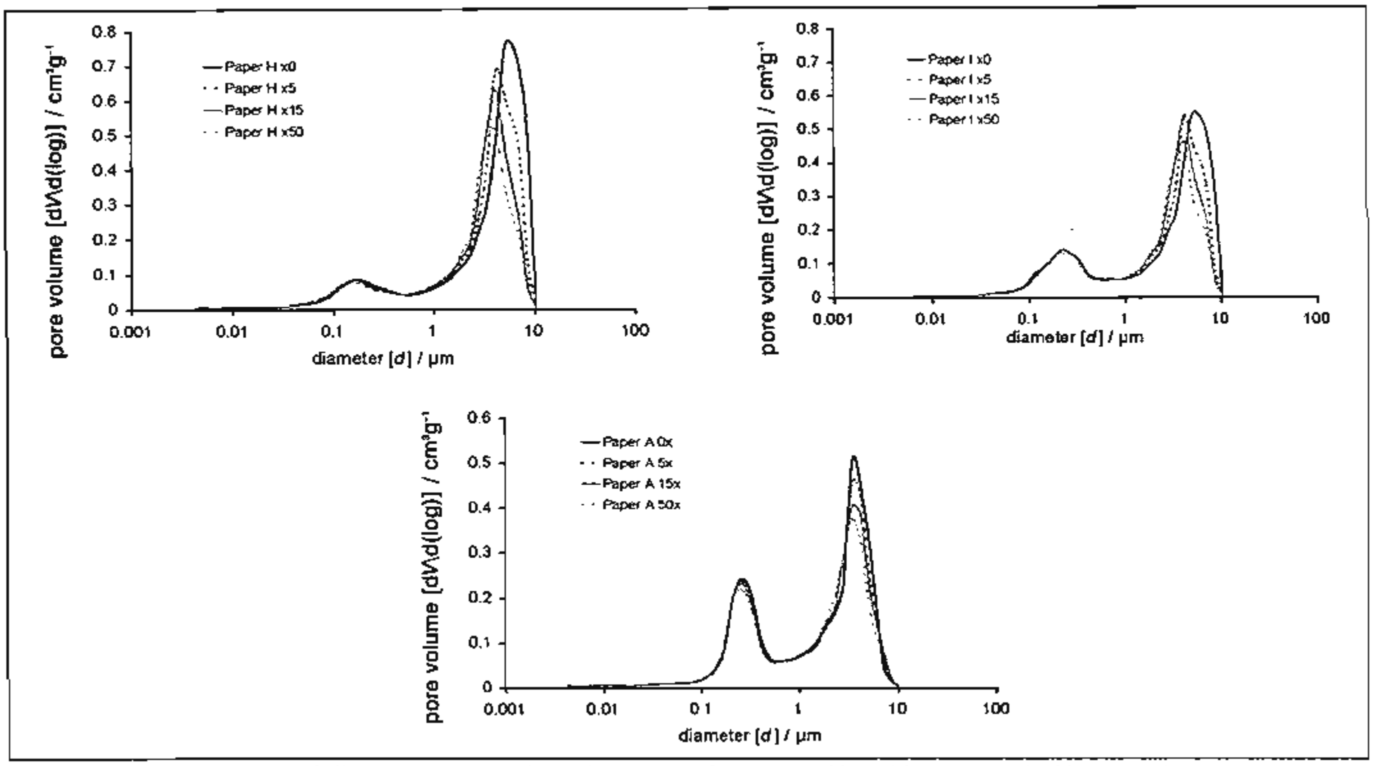


Figure 32 Differential mercury intrusion curves for papers H and I compared with paper A.

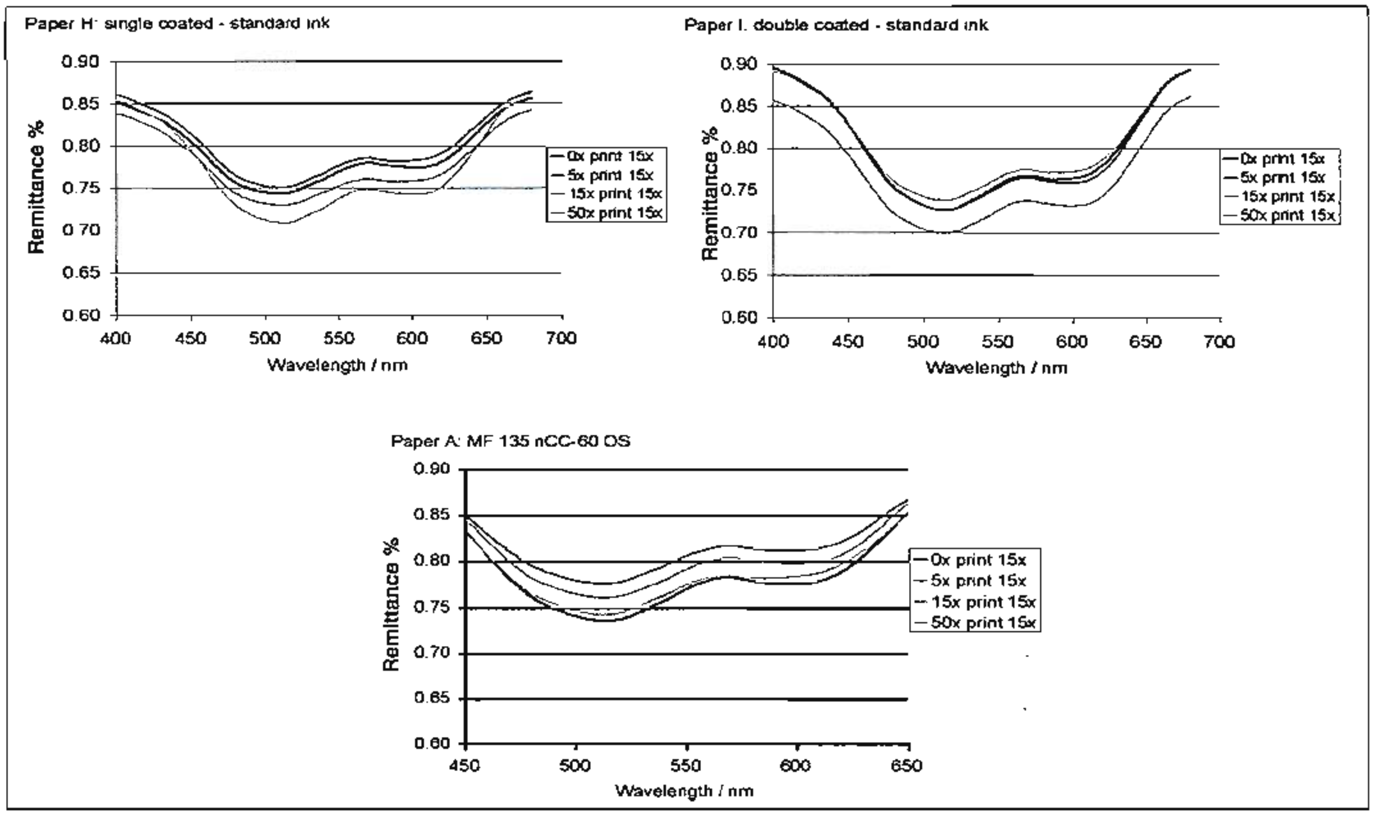


Figure 33 Remittance values of stay open ink on papers H and I compared with paper A.

The single coated paper H shows a deterioration in print rub resistance after 50 pre-rub passes. The double coated sample I deteriorates after 15 pre-rub passes but at 50 pre-rub passes has recovered. The further compression has generated some more fine pores, which then compensate for the increased contact area. This is the inverse to paper A, on which, after the initial pre-rub passes, print rub improved but then at 50 pre-rub passes the print rub returned to its initial level. In this case of paper A the higher contact area together with the lack of response from the basepaper to pre-rubbing was the determining factor in the poor print rub resistance.

Spectroscopic remittance values are compared between the print rub transfer sample and the original pre-rubbed paper, i.e. the remittance difference between the background pre-rubbed paper and the transferred print rub sample of ink onto fresh paper undergoing the number of print contact rubs in *Figure 34*. The graphs compare the 3 paper types, where the spectra are defined as {Remittance of background paper - Remittance of print rub contact paper}.

Paper H had the lowest surface roughness as measured by CLSM. This paper is seen here to have the least print rub off. Paper I has the highest level of print rub and is the double coated paper. After 50 pre-rub passes all the samples are of a comparable quality.

## Interim finding III

As soon as the pre-rubbing technique was applied to the double coated paper the print rub increased. The basepaper is being only slightly compressed, whilst the contact area is being increased. The single coated quality showed by far the best print rub resistance, partly because the compressibility of the basepaper can be better utilised under contact deformation and partly because for the same coat weight application there are many more fine pores in the coating volume compared with a double coated paper having larger pores in the precoat, i.e. despite the double coated sample being overall more porous.

Finally, if the basepaper is of poor quality in respect to print rub (incompressible), then using more coating will not improve the print rub resistance, but only make it worse. In such cases single coating is probably preferable.

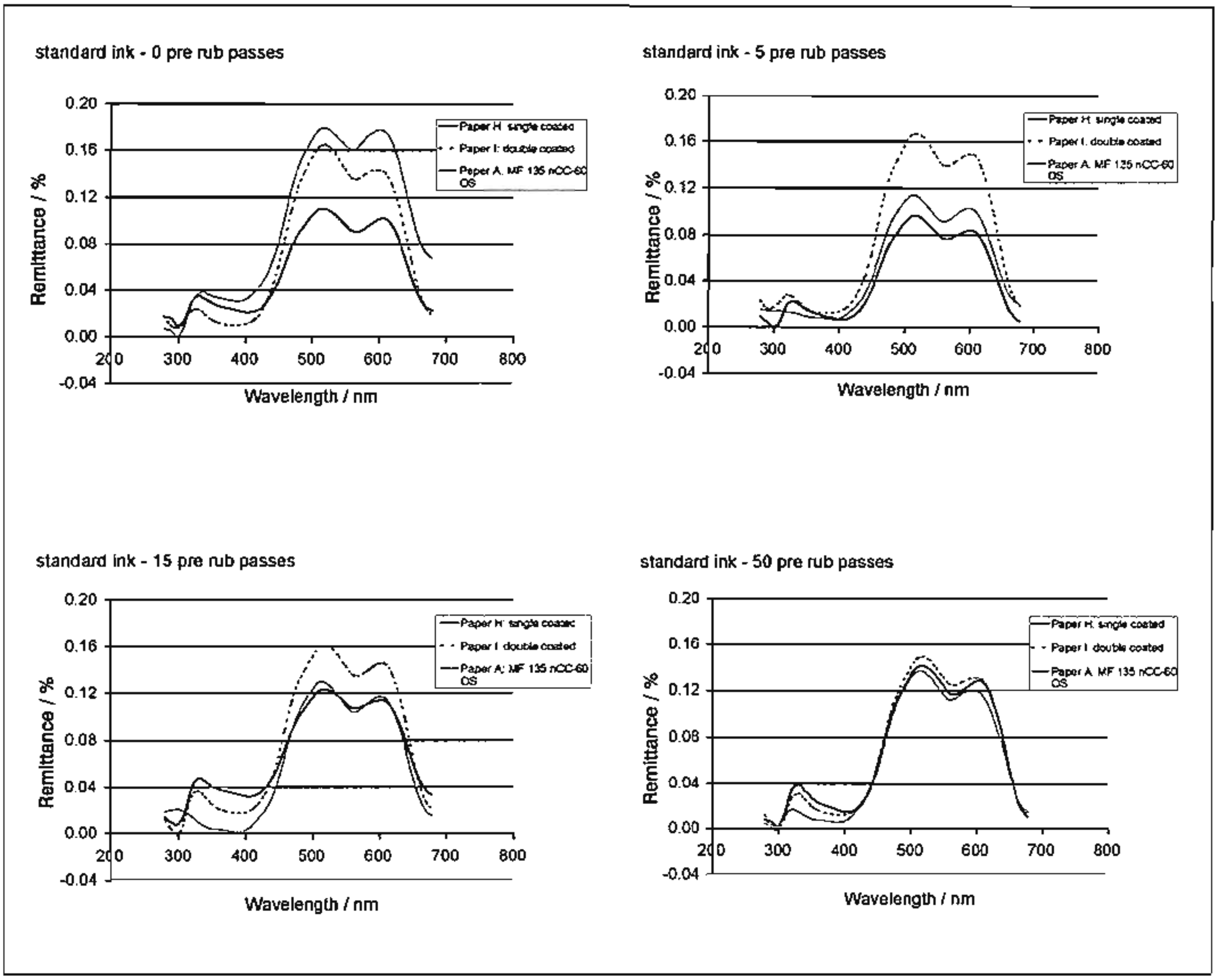


Fig. 34 Remittance difference values of stay open ink on papers H and I compared with paper A.

## Conclusions

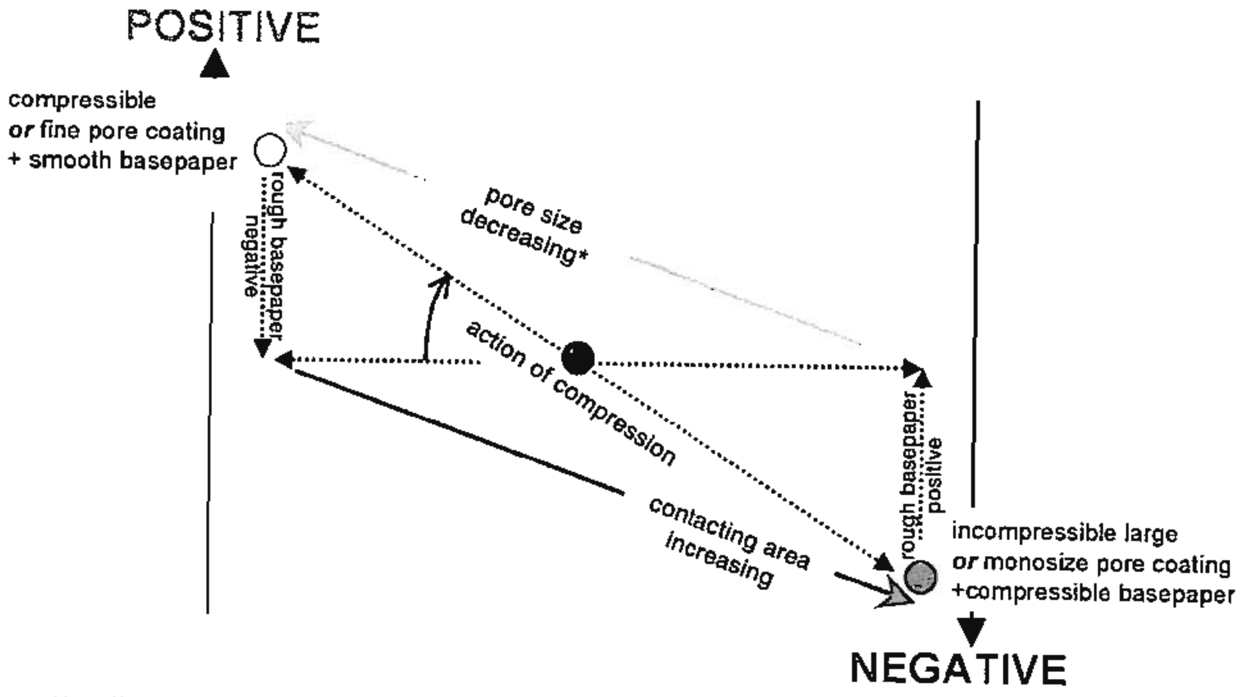
We now draw the interim findings in sections I-III together in the form of a schematic representation, *Figure 35*, showing graphically the action of compression on basepaper and coating, together with the coating structure design. It displays a balance: too much compression of the basepaper without additional fine pores in the coating is bad, as contact area increases and the ink has not undergone sufficient capillary-driven setting. If, however, sufficient fine pores exist, then compliant basepaper is good. Large or monosize pores are generally bad, as capillary forces are low and the surface area for adsorption and chromatographic oil separation is limited. A rough basepaper makes the print rub relatively insensitive to the coating structure, and leaves it on a medium level, but not at the best achievable.

A summary of the trends that can be used to control print rub can be given as follows:

- Decreasing the pore size in the surface paper coating structure, and thereby increasing capillarity and adsorbing surface area, has a positive effect on print rub resistance (green line), with the provisos that:
    - o Increasing the contact area can have a negative effect on print rub (red line) if the coating lacks capillarity, i.e. the fine pores are absent and the coating has large or monosize pores only.
    - o Compressible basepapers can best manifest their benefit when the coating is not rigid, i.e. precoats tend to mask basepaper benefits.
- Rough paper can only lead to compromise! If a coating structure has fine pores, but the base paper is rough, then the benefits of the fine pore structure are lost. A rough basepaper will, however, reduce the contact area and thus reduce any deficits there may have been from poor coating design.

If it is not possible to form fine pores in a coating structure to aid the ink vehicle absorption, and hence complete ink setting and permit drying, then it is necessary to avoid increasing the contact area and thus avoid smoothing the paper too much. A larger contact area will lead to more ink transfer and, hence, an increase in print rub tendency. If, however, fine pores can be created their advantage overrides the negative impact of higher contact area and so better ink setting, drying and rub off resistance, can be achieved.

**Basepaper and coating pore structure factors controlling print rub:**
**compressibility makes bad coating worse ●, good coating better ○!**



*Note: The term ***pore size decreasing*** refers to increased absorption and adsorption potential via increased capillarity and pore surface area, and/or by increased intra latex-polymer diffusion.

Figure 35 Basepaper and pore structure factors controlling print rub

## Appendix

Paper A: MF 135 nCC-60 (where MF refers to machine finished and nCC-60 is a narrow particle size gcc having 60 wt% < 1 $\mu$m applied in the pre and topcoat)

Paper B: MF 135 bCC-75/Finegloss (where bCC is a broad particle size gcc containing 75 wt% < 2 $\mu$m, and Finegloss contains 80 parts by weight of fine gcc (95 wt% < 2 $\mu$m) and 20 parts by weight of fine US glossing clay in the topcoat applied to the same precoat as paper A)

Paper C: a matt paper containing satin white in the formulation

Paper D: a semi-matt, adopting different coating-basepaper combination

Paper E: commercial matt

Paper F: as Paper E but finished to semi-matt

Paper G: example of non-stretching matt paper

Paper H: 50 parts bCC-75 and 50 parts Finegloss + Acrylic binder, single coated

Paper I: 50 parts bCC-75 and 50 parts Finegloss + Acrylic binder, double coated

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