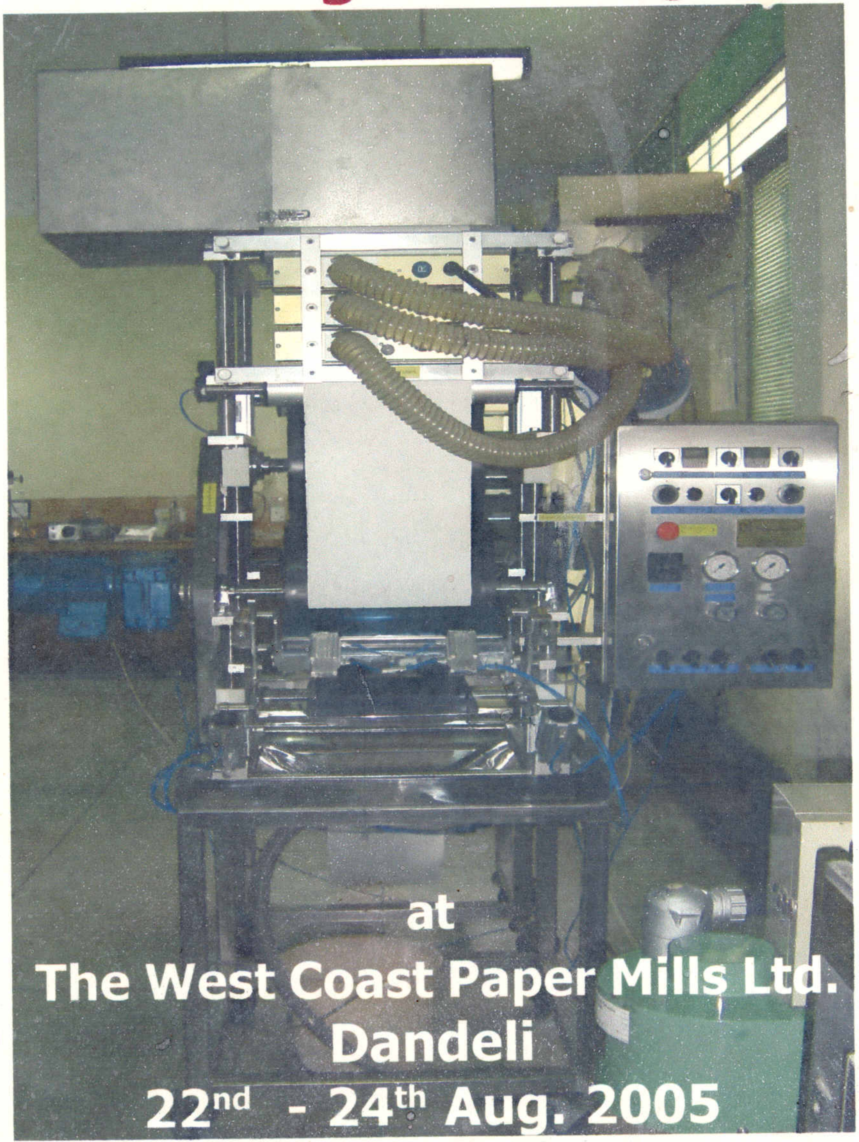
5th Cess Training Programme

on

Sizing & Coating



at

The West Coast Paper Mills Ltd.

Dandeli

22nd - 24th Aug. 2005

Sponsored by

Development Council for Pulp,
Paper & Allied Industry

Ministry of Commerce & Industry
Govt. of India

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Organised by

केन्द्रीय लुग्दी एवं कागज अनुसंधान संस्थान
Central Pulp & Paper Research Institute
AN ISO 9001-2000 INSTITUTION
In pursuit of cleaner production, resource conservation & quality excellence

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AN ISO 9001:2000 INSTITUTION
In pursuit of cleaner production, resource conservation & quality excellence
An autonomous organisation registered under societies Act under the administrative control of the Ministry of Commerce & Industry (Govt. of India)

Accredited by Member of the IAF MLA for QMS
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Dr. A. G. KULKARNI
Director

PREFACE

After an overwhelming response from the Industry and also from the external Faculty members and great success of the four Cess Funded Training Programmes organized by Central Pulp & Paper Research Institute, Saharanpur (UP) during 2002-2005, it was decided by the Cess Committee that CPPRI should also organize four more such regional training programmes near the locations close to mill sites.

The fifth cess funded training programme on "**Sizing & Coating**" is the first such program which is being organized at a mill site i.e. The West Coast Paper Mills Ltd., Dandeli (MS) from 22nd to 24th August ,2005. The topic chosen for this training programme is very relevant to paper industry looking into the remarkable developments which have taken place during the last two decades. It is important for the mill's personnel to know about these developments, and how best they can utilze these developments in their mills for improving the productivity, product quality and also the cost effectiveness. Institute has the privilege of having senior faculty members drawn from the industry & academic institutions, who will share their wide experience along with the recent developments which have been adopted in the different pulp & paper mills in the country

A team of dedicated young Scientists of the Institute have worked hard to make this training programme useful & meaningful through selective "**Lectures & Demonstrations**". The training **MANUAL** covering the articles by various faculty members from the Department of Paper Technology (IIT, Roorkee), CPPRI and industry is a comprehensive one and should be an useful tool for the participants to implement the new technological development in their respective mill.

I wish to record my sincere thanks to **Sh. B.S. Mundra**, President (Technical) & Management of The West Coast Paper Mills Ltd., for extending all cooperation & assistance in organizing the first ever-training program at a mill site. I also thank **Dr. Vasant Chapnerkar**, an eminent Scientist from U.S.A. who accepted our request to be a faculty at a very short notice.

I am sure that this training programme will give the required exposure to mill's personnel in these two important areas. I wish the training programme a success.

(A.G. Kulkarni)

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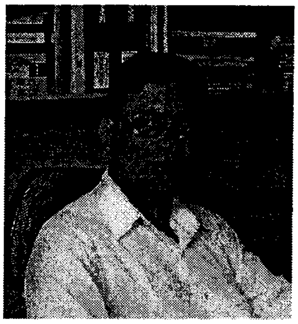
TRG PROGRAMME ON SIZING & COATING, AUG 22-24, 2005

STATUS OF INDIAN PAPER INDUSTRY

CENTRAL PULP & PAPER RESEARCH INSTITUTE

PRESENT STATUS OF THE PAPER INDUSTRY



Dr. A. G. Kulkarni,
Director, CPPRI

About The Author

Dr. A.G. Kulkarni, Director Central Pulp & Paper Research Institute (CPPRI) Saharanpur, Uttar Pradesh, India has been with the CPPRI since its inception. He holds a Master degree in Chemistry & Doctorate in Black Liquor and Lignin Chemistry.

Dr. Kulkarni has pioneered the research work on Desilication of black liquor with eventual development of mill scale plant, installed at Hindustan Newsprint Ltd., Kerala and High Rate Bio-methanation of black liquor rich effluent and a mill scale unit is successfully operating at Satia Paper Mills is another achievement of Dr. Kulkarni. His contribution in the area of physico chemical & thermal properties of agro - residue non-wood black liquors has now made it possible to process this liquor in chemical recovery boilers. He has published more than 300 scientific papers in Indian and International journals. He is widely traveled in Europe, S. E. Asia, and Australia and has been on several foreign missions as UNDP/UNIDO Consultant.

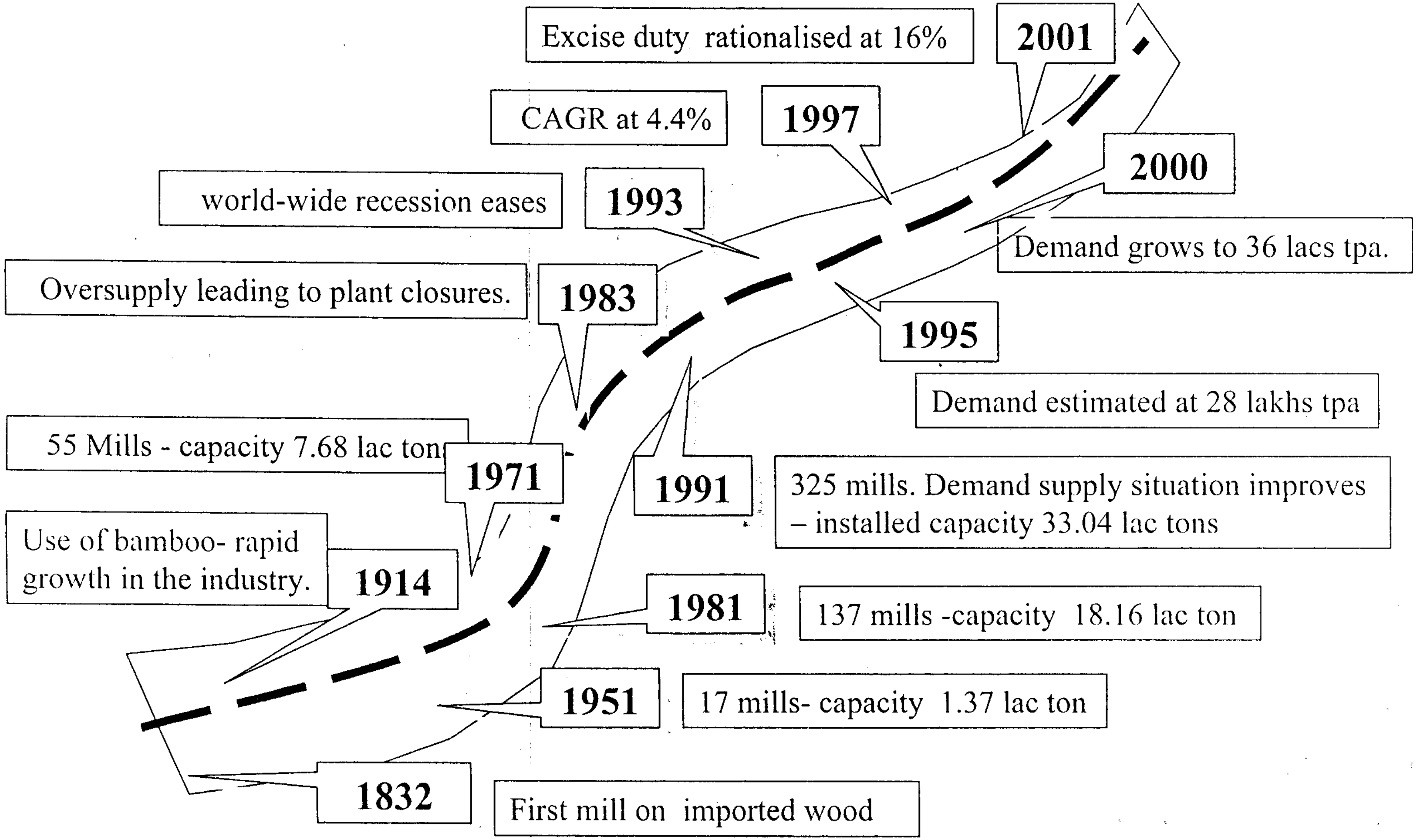
His areas of specialization include pulping and bleaching, black liquor-its chemistry & processing, environment and energy management. Dr. Kulkarni holds several patents-important ones being on desilication of black liquor, thermal treatment of black liquors and Direct Alkali Recovery System etc. He is a member of several National and International Scientific & Technical organizations and also on board of Directors of Paper Mills & Research organizations

PRESENT STATUS OF THE PAPER INDUSTRY

A.G. Kulkarni

The article discusses the chronological developments in Indian Paper Industry in terms of its growth, production level and levels of capacity utilization. The information also provides the technological status of our industry in terms of trends available on raw material and basic input requirement along with the cost involved. The technological development in pulping and bleaching, paper machine, and also focus on the energy and environment in various categories of the mills, has been addressed.

Indian Paper Industry : The Road Map from 1832 to 2001



1832 First mill on imported wood

1914 Use of bamboo- rapid growth in the industry.

1951 17 mills- capacity 1.37 lac ton

1971 55 Mills - capacity 7.68 lac ton

1981 137 mills -capacity 18.16 lac ton

1983 Oversupply leading to plant closures.

1991 325 mills. Demand supply situation improves – installed capacity 33.04 lac tons

1993 world-wide recession eases

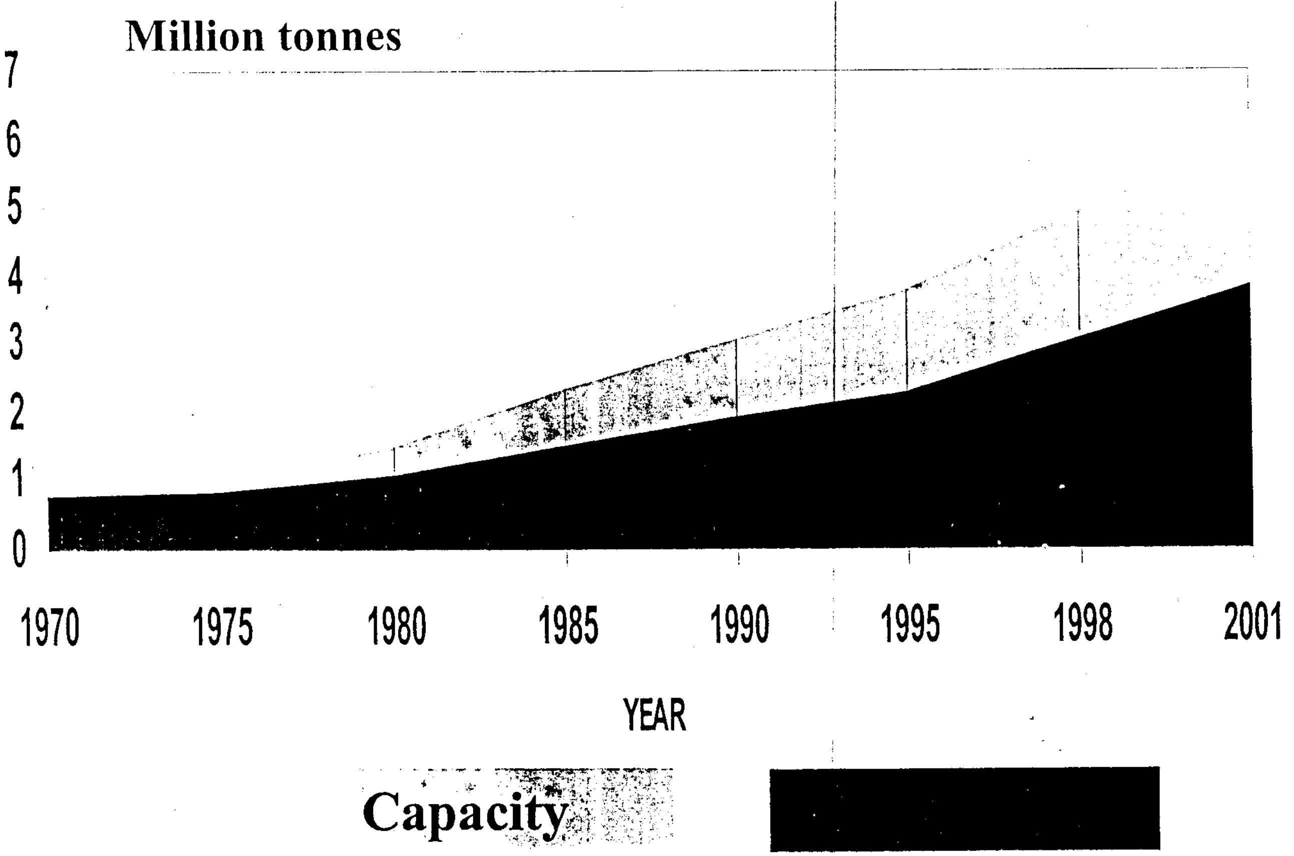
1995 Demand estimated at 28 lakhs tpa

1997 CAGR at 4.4%

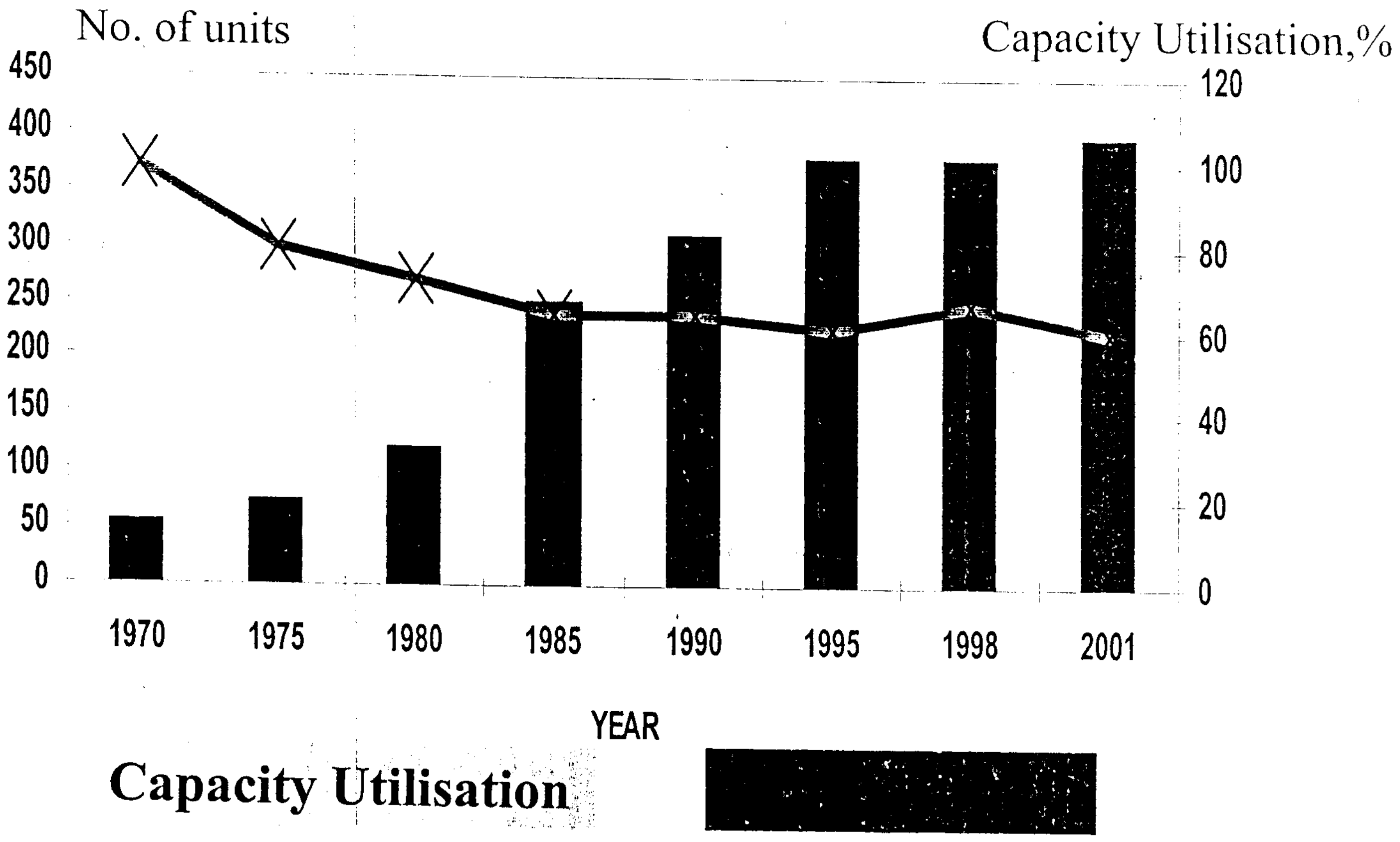
2000 Demand grows to 36 lacs tpa.

2001 Excise duty rationalised at 16%

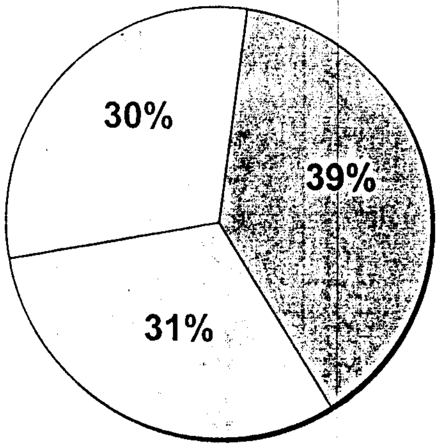
Growth of Indian Paper Industry Installed Capacity & Production



GROWTH OF PAPER INDUSTRY - CAPACITY UTILIZATION & NUMBERS

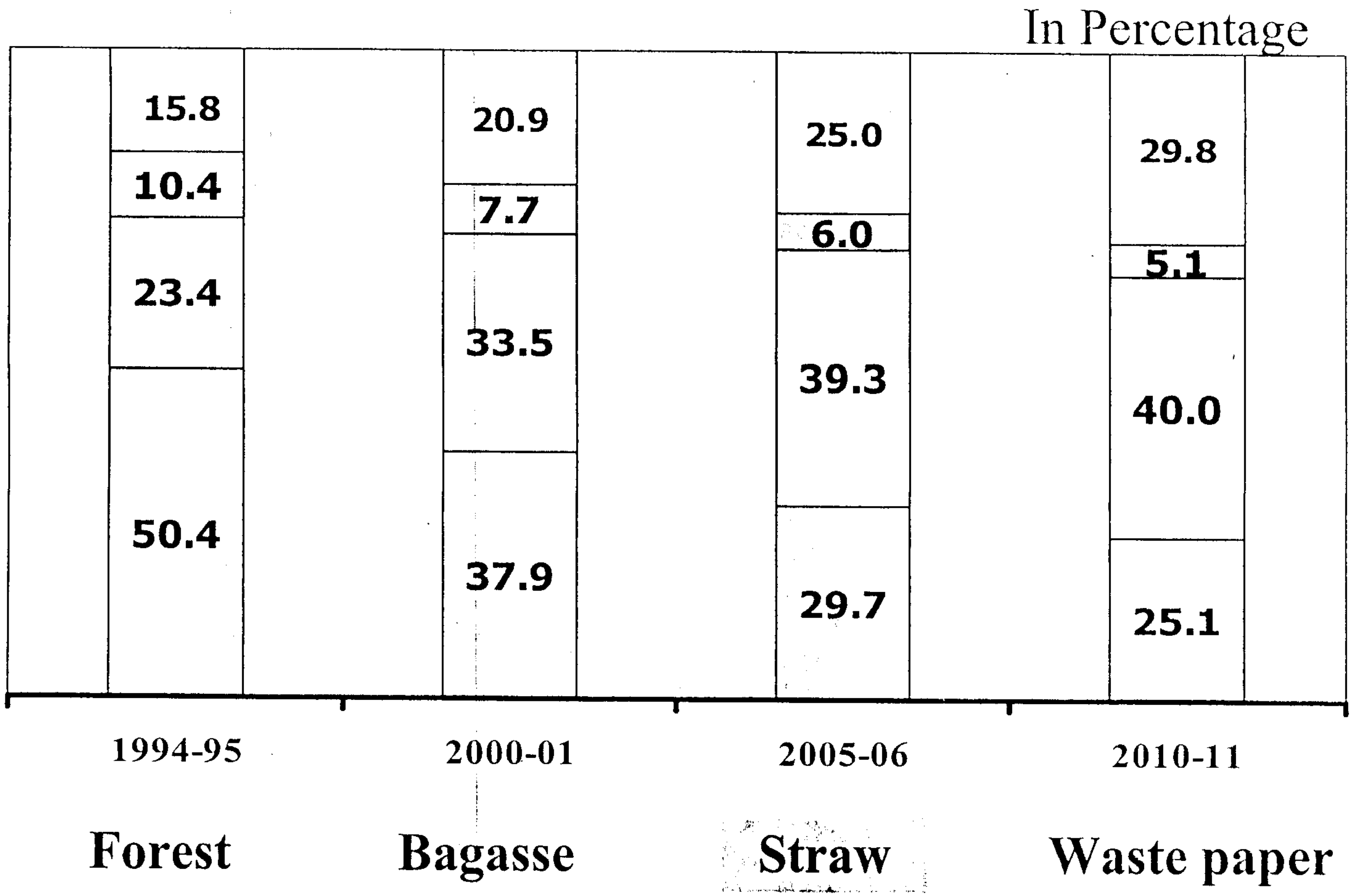


Indian Paper Industry : It's Structure

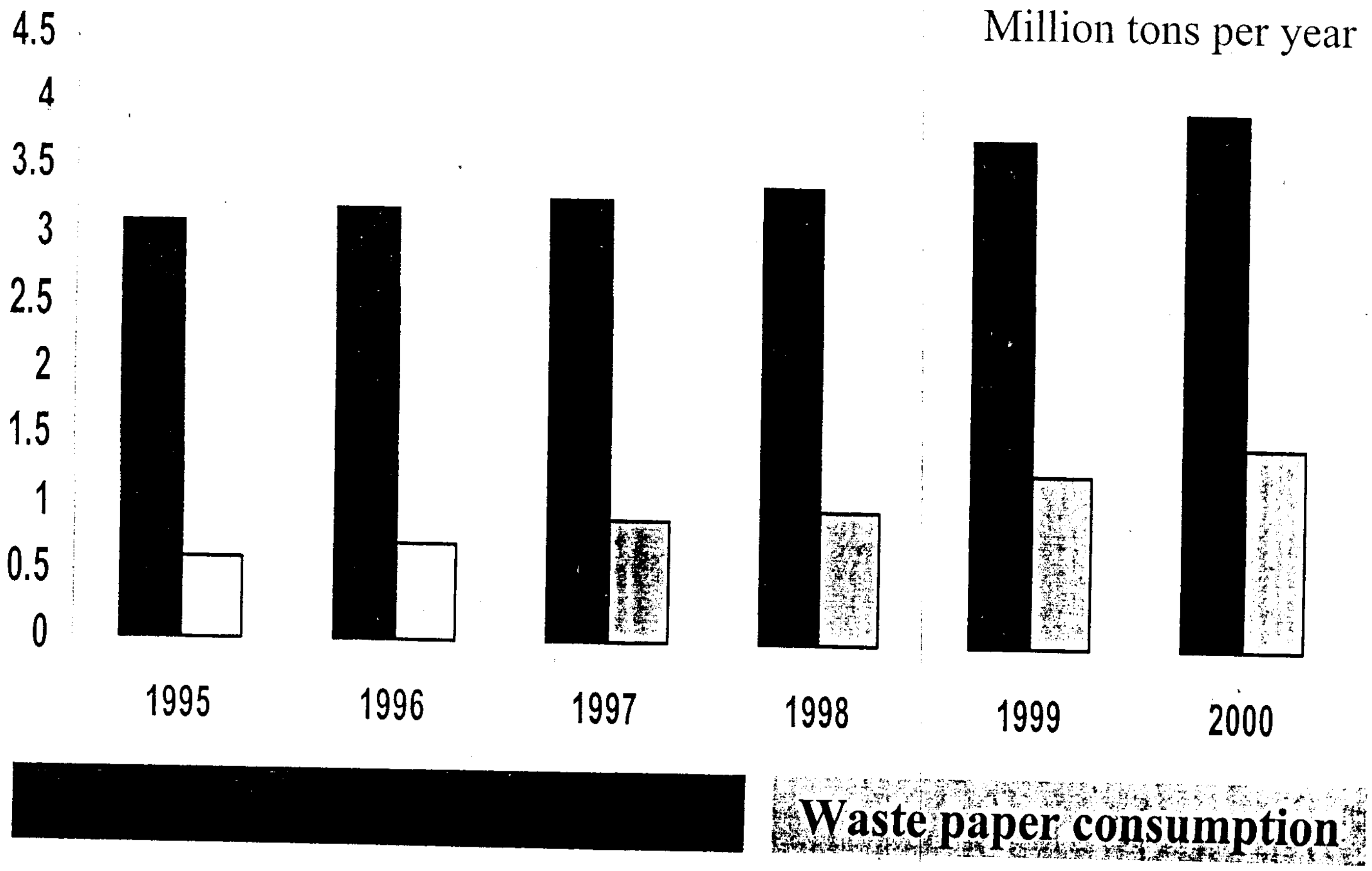


Data	Sector			Total
	Forest based	Agro Based	Recovered Paper	
No.of Mills	28	131	241	400
Installed, Capacity Mn tons/yr.	2.4	2.1	1.9	6.4

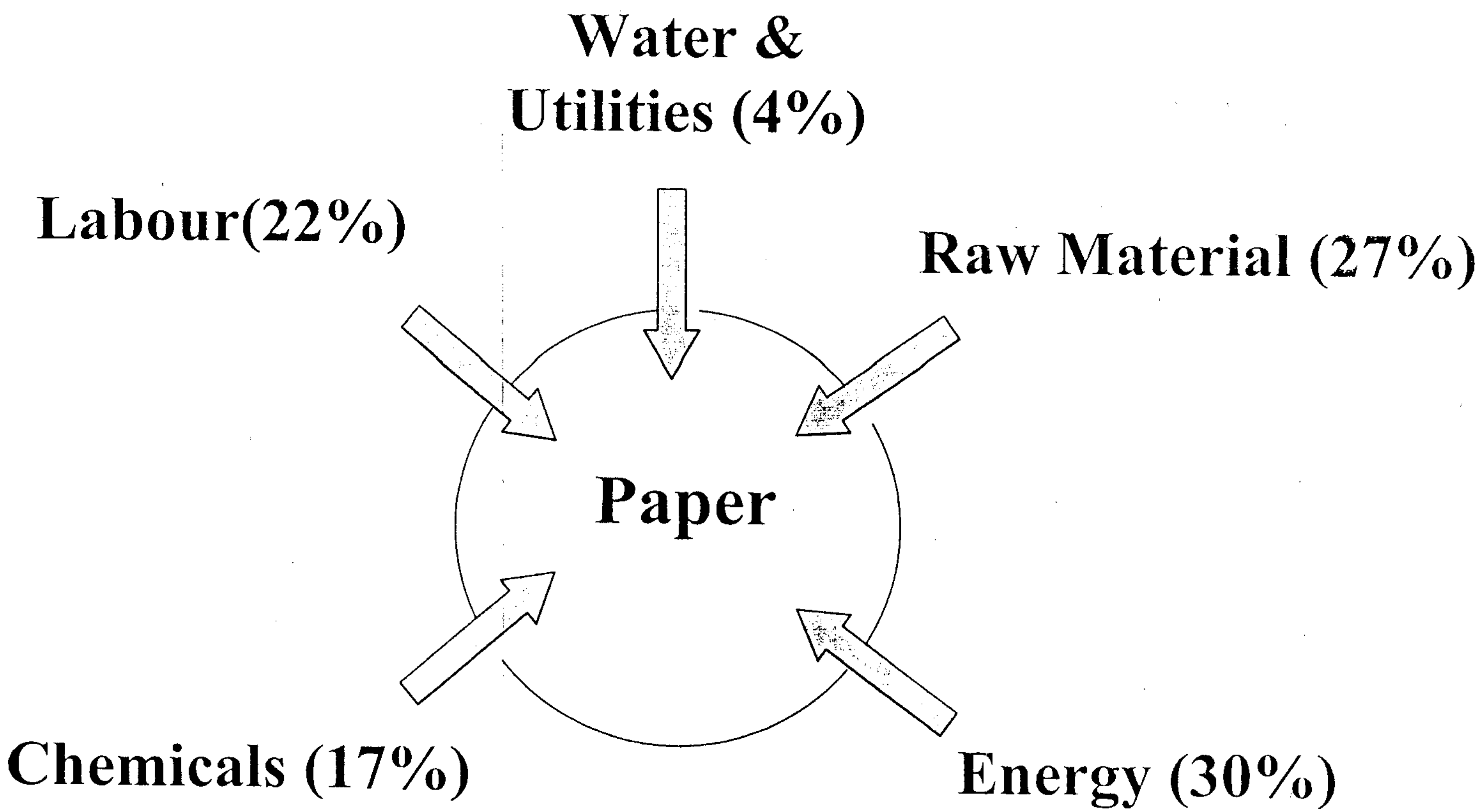
Paper Production from Fibrous Raw Materials



Share of Waste Paper in Total P & B Production (1995 - 2000)



Basic Inputs



Water &
Utilities (4%)

Labour(22%)

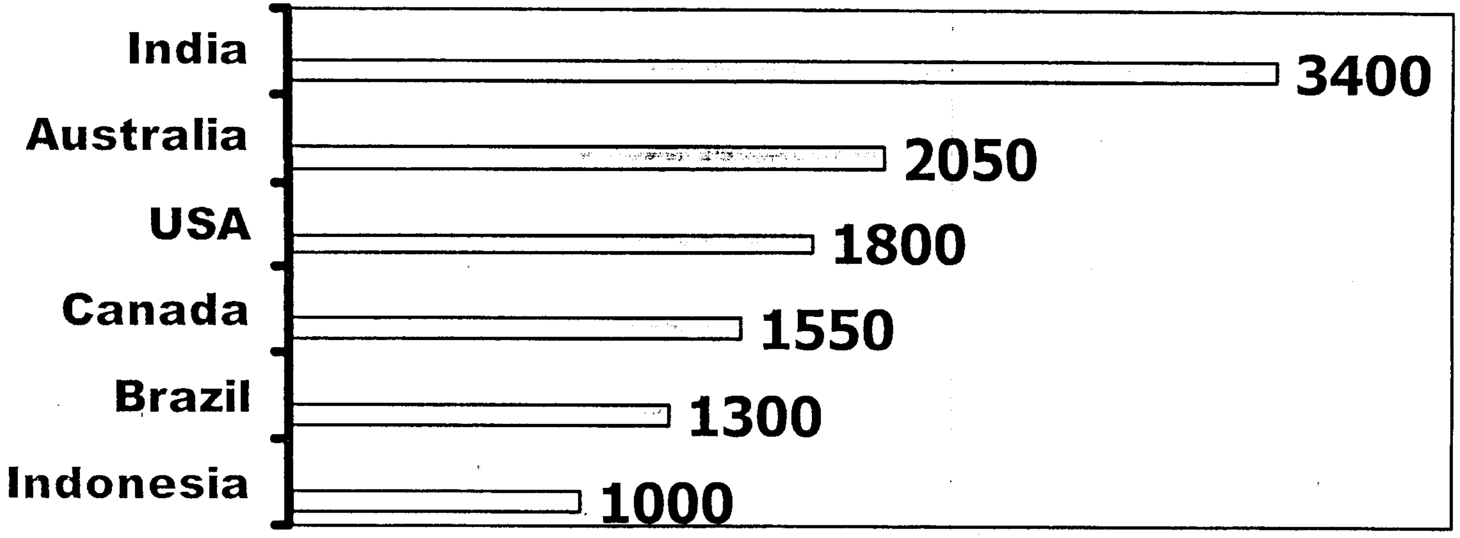
Raw Material (27%)

Paper

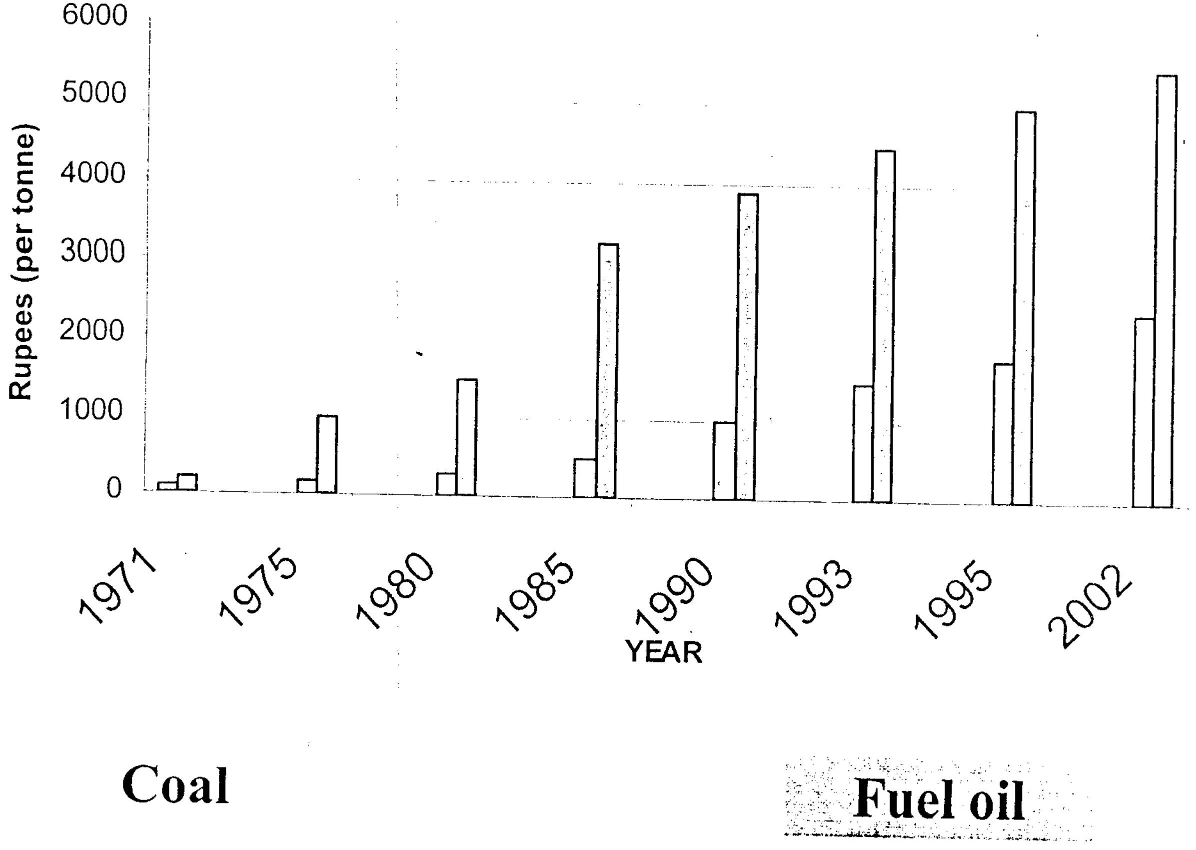
Chemicals (17%)

Energy (30%)

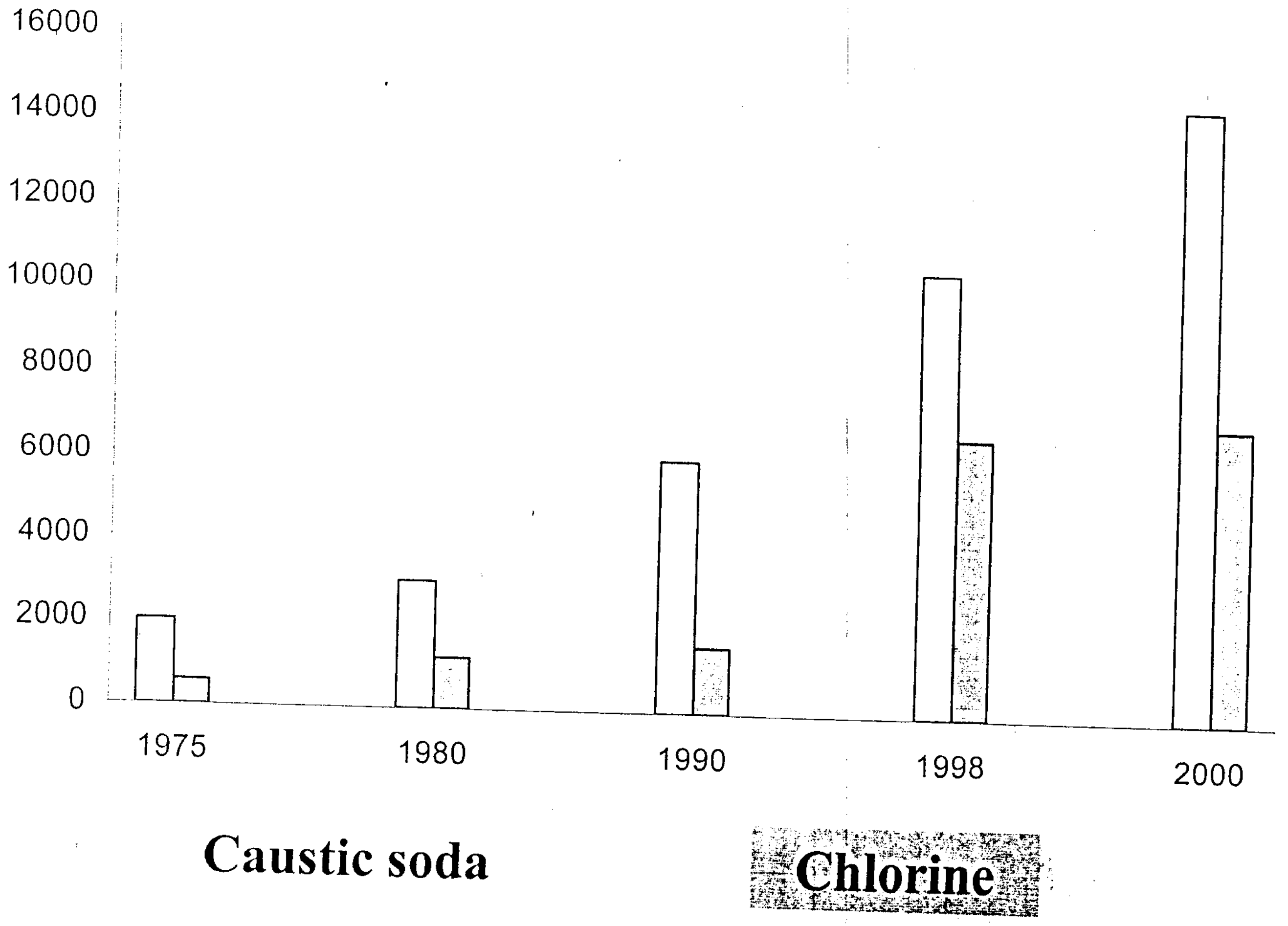
Raw Material Cost (Rs per Ton)



COSTS TRENDS OF COAL & FUEL OIL



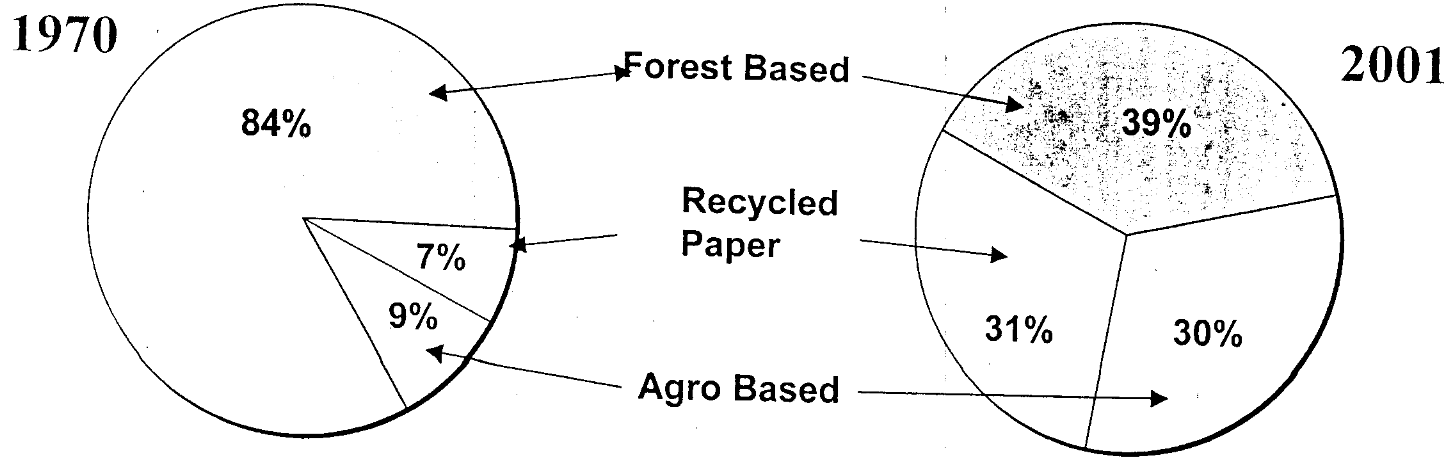
TREND IN RISE IN COST OF CAUSTIC SODA & CHLORINE



[redacted]

- Sustained raw material availability.
- Inadequate infrastructure.
- Uneconomic scale of operation.
- Obsolesence of technology in most cases.
- High cost of basic inputs.
- Eco friendly state of art processing technologies.

Raw Material : Change in Trends

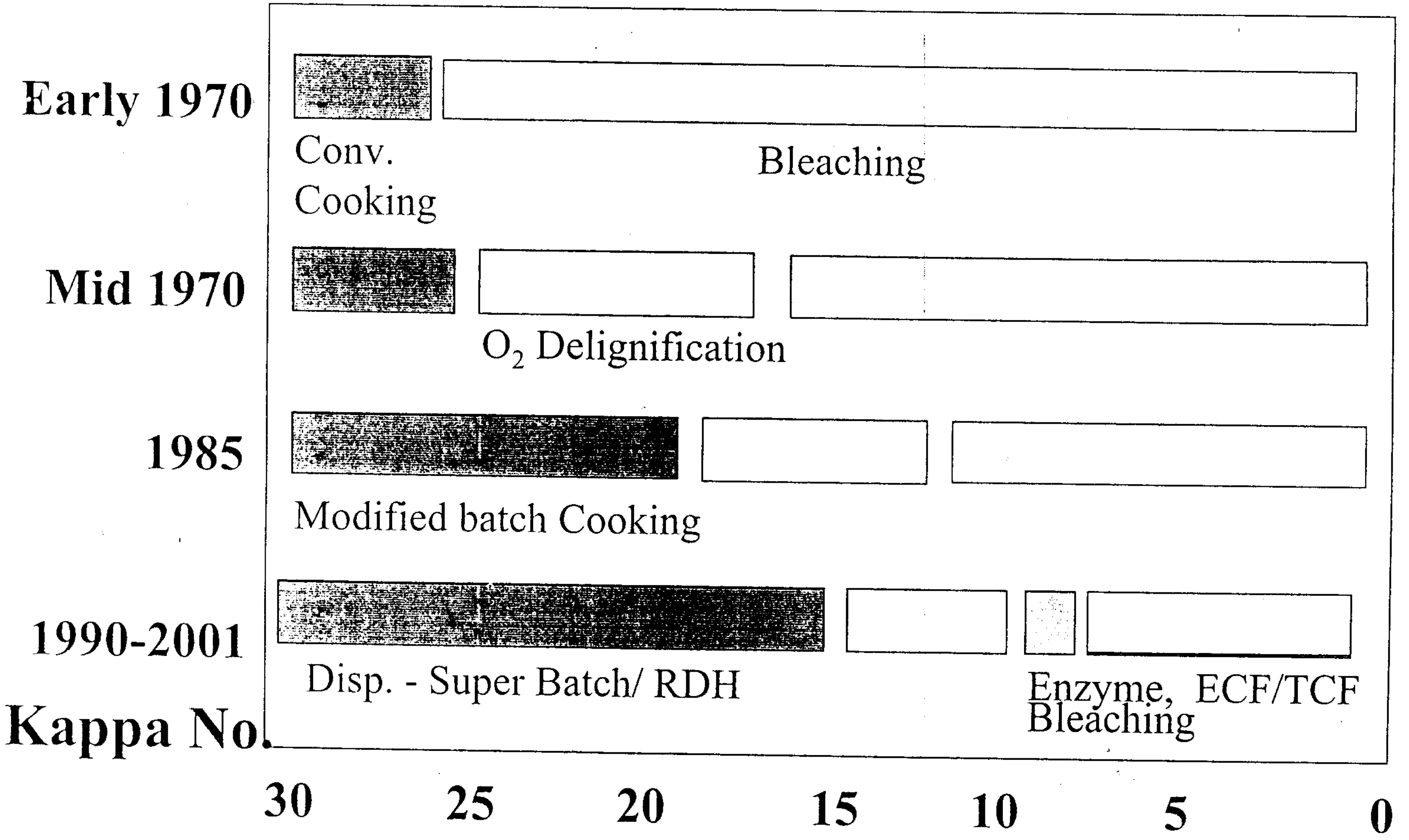


Data	Year	
	1970	2001
Registered Units	57	400
Production, Million tons/yr.	0.77	3.85

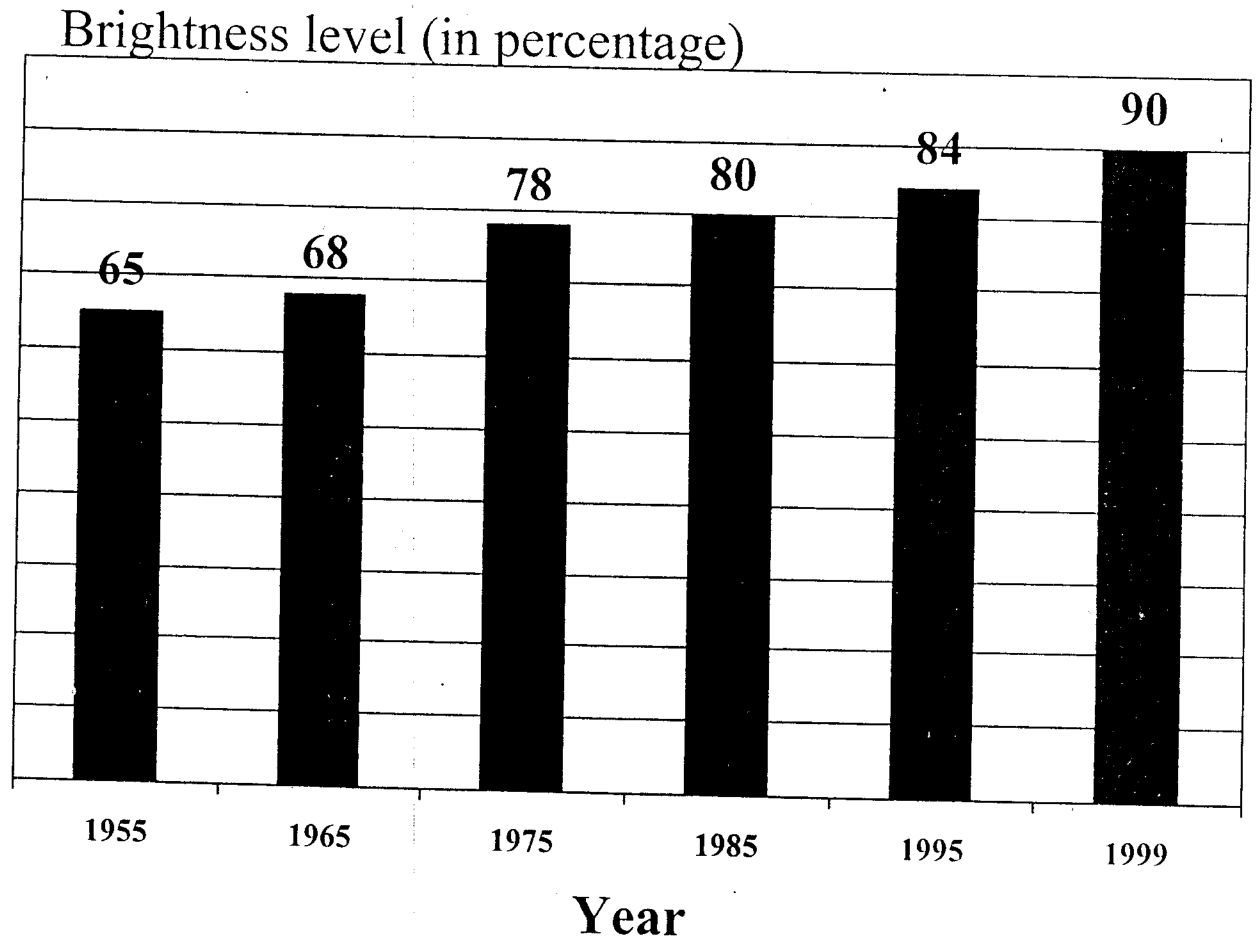
[redacted]

- Improved Raw Material Handling & Cleaning.
- Continuous/ Modified Batch Digesters.
- State of Art Washing Systems.
- Elemental Chlorine Free Bleaching.
- Omission of Direct Contact Evaporators.
- Lime Sludge Reburning System.
- Improved Solid- Liquid Separation Techniques.
- Energy efficient Effluent Treatment practices.

Pulping & Bleaching Scenario
(1970-2001)



Brightness Level of Paper



Large Paper Mills

- Higher water usage & energy discharge of colored effluent
- Toxic emmissions of chlorinated organic compound (AOX).
- Solid waste generation – Lime sludge & Fly ash.

Medium & Small Paper Mills

- Higher AOX generation.
- Lack of chemical recovery leading to energy & chemical losses.
- Inefficient equipments leading to high utilities.

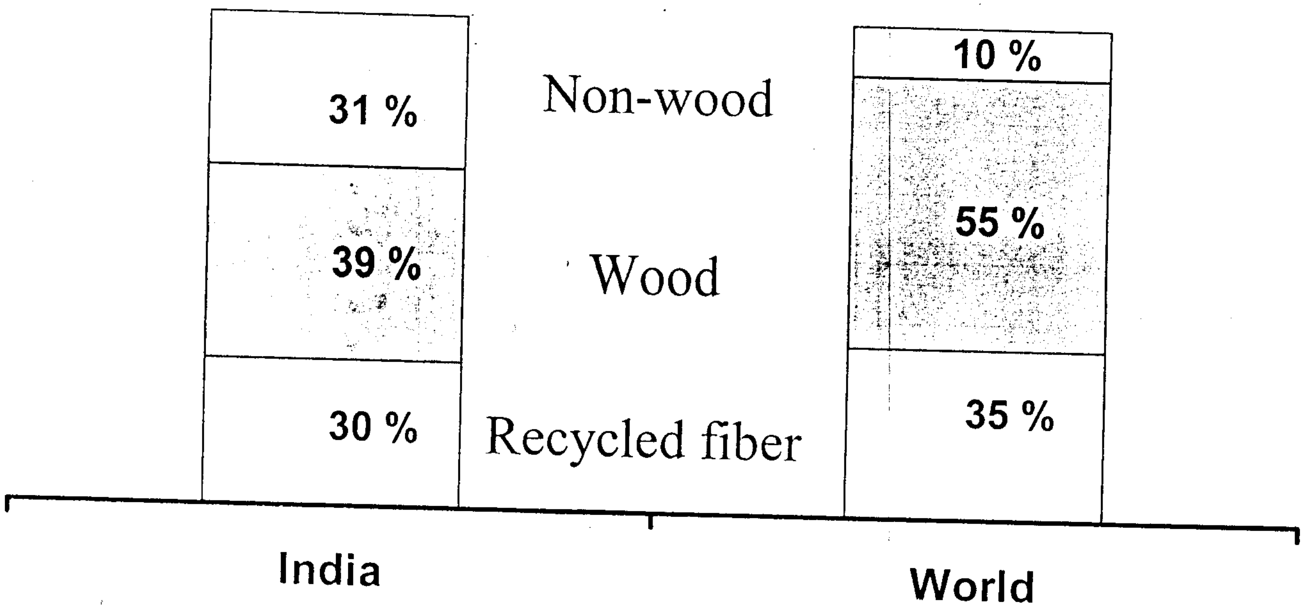
AOX DISCHARGE LEVELS : SEGMENT WISE

TYPE OF MILL	AOX LEVEL kg/T PAPER
RAYON GRADE PULP	<0.5
NEWSPRINT PULP	<0.5
LARGE PAPER MILL	1.0 – 2.5
MEDIUM & SMALL MILLS	4.0 – 6.5

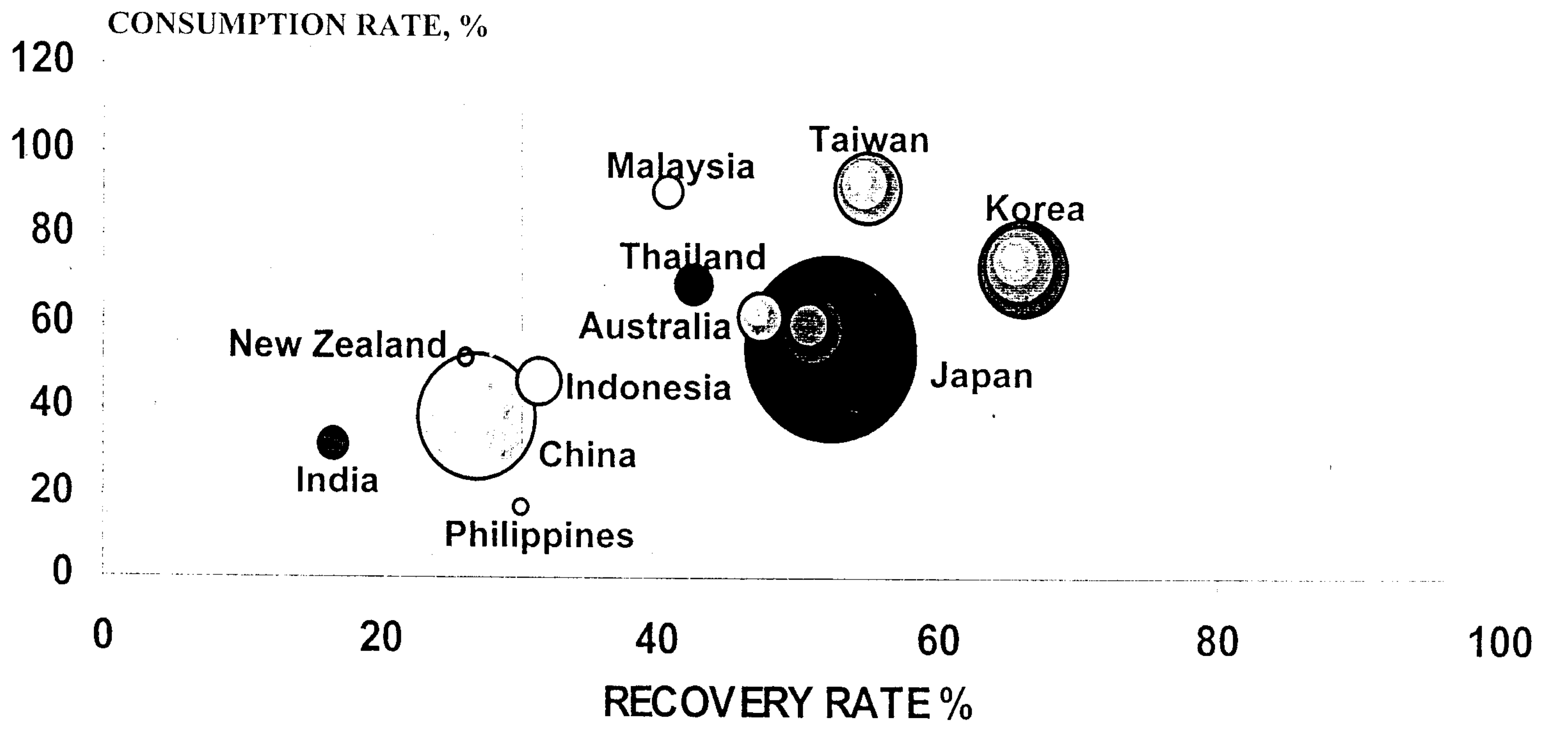
India Vs World : An Overview (2000)

Parameter	**India**	**World**
Installed Capacity, Million tons/yr.	5.4 ( )	364
Average size, tons/yr.	13,300	41,000
Production, Million tons/yr.	3.9	323
Production Growth Rate,%	4.6	2.6
Per Capita Consumption, kgs	4.0	54.0
Consumption Growth Rate,%	3.5	2.9

Raw Material



Waste Paper Consumption & Recovery

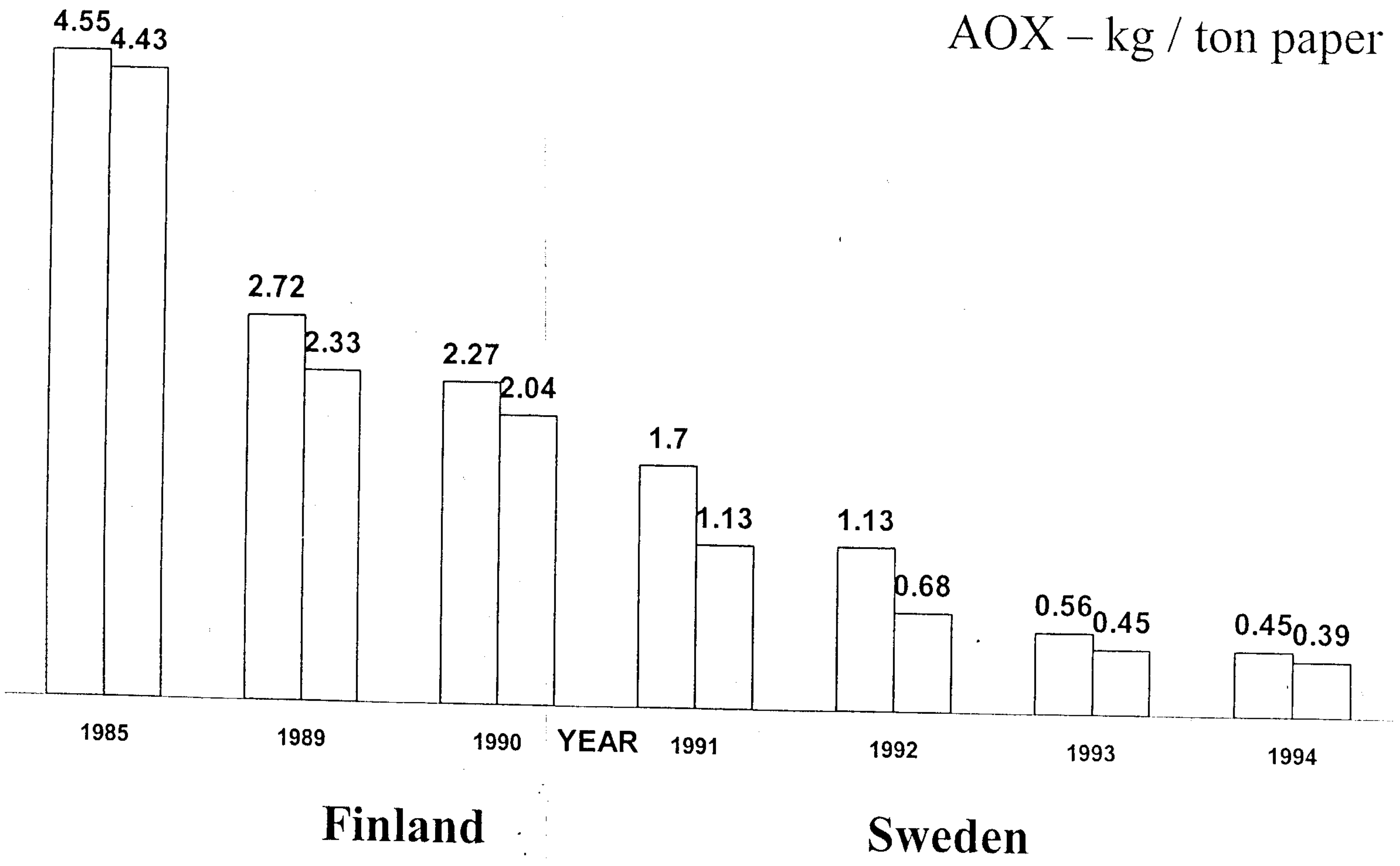


Bubble size is a function of waste paper recovery in tonnes

Consumption of Basic Inputs

Input Norms (per ton basis)	Mills in India	Mills Abroad
Raw material, tons	2.0- 2.4	1.8-2.0
Energy, GJ	23-37	18-22
Water, m^3	150-250	50-100
Chemical Recovery,%	88-94	95-98
Manpower,nos.	14-20	5-7
Technical manpower, no.	2	4

DEVELOPMENT OF AOX DISCHARGES FROM PULP AND PAPER INDUSTRY



Paper mill structure in India 2001

There are over 500 paper mills in India. Most of the mills are small, only 34 mills have a capacity of over 33 000 tons. The Indian paper machines are mostly small units. In an international comparison, even the largest machines are medium-size, as large-scale machines are today in the range of 400 000-600 000 t/a, and have a trim width up to 10 metres.

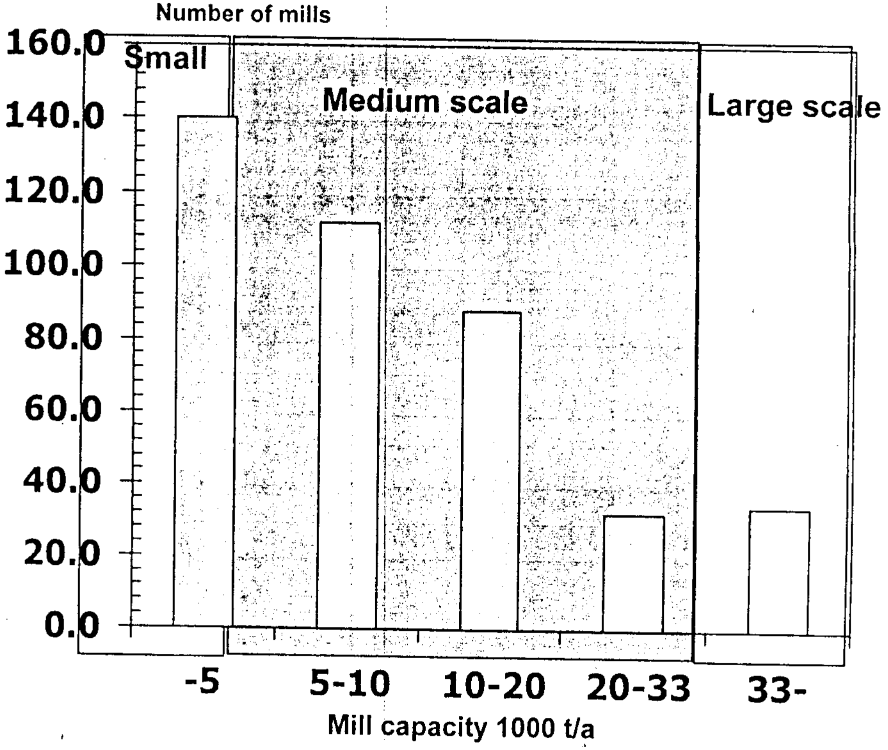
The following parameters are illustrative of the Indian paper industry:

The average capacity of paper machines is about 14 000 t/a

Most of Indian paper machines have a trim width from 1.5 to 3.5 m

There are only 9 paper machines with trim width of 5 m or more

Only 14 machines have capacities 50 000 t/a or more



PM size and speed - economy of scale

Mills and machines are relatively small in India, technology is outdated and quality of raw materials and end products is low.

- Average and maximum mill and machine capacities are small in India. **New machines should be about 50 % of international size**.
- With bigger machines investment costs, production of utilities, effluent treatment and all fixed **costs would be lower per produced ton of paper**. Especially bigger machines can afford better automation (QCS and DCS).

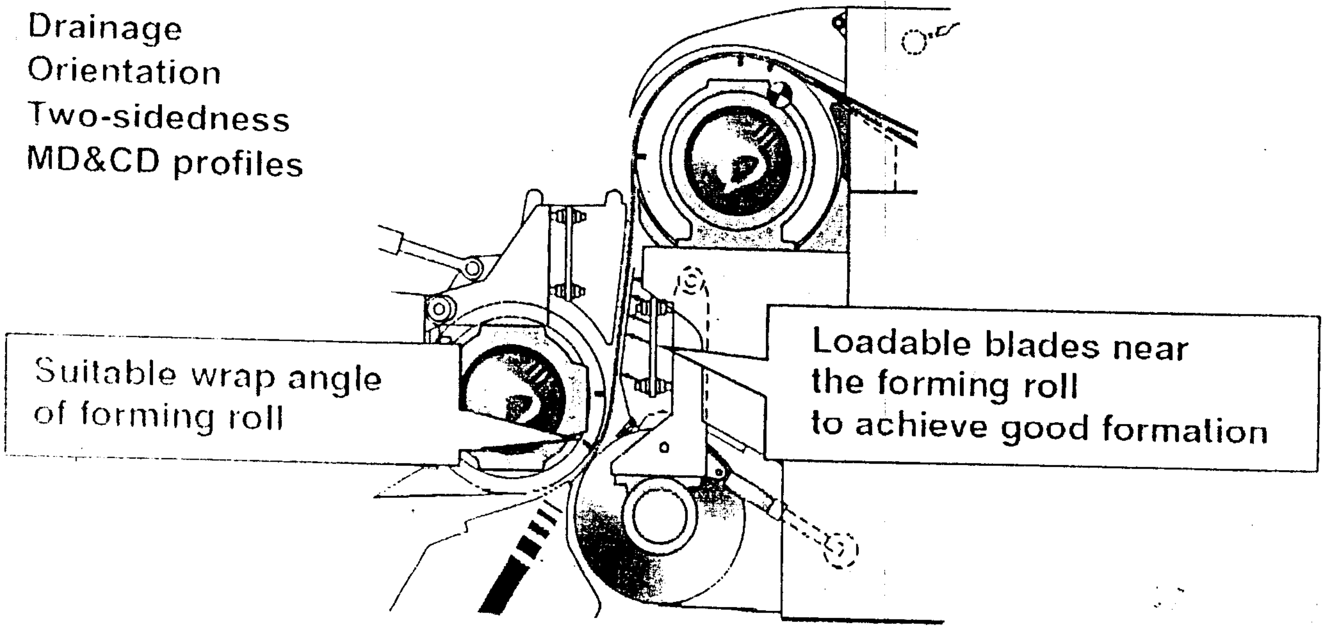
- **High speed machines** (>1000 m/min) are needed for cultural papers and one-layer boards. With a higher design speed, technology and paper quality will be closer to the international standard. Machine width can be less than internationally.
- To be internationally competitive **second hand machinery should be imported very selectively**.
- Machines representing old-dated technology should be **gradually shut down**.
- Mills and machines have to focus on **few grades** to be more effective

High speeds – better quality with gap former

Project Number 52A0087
Final Report

There are only some twin wire machines in India. Best roll and blade gap formers improve paper quality and drainage, which are important for paper made of Indian raw materials. Roll and blade gap formers give a good combination of the following properties:

Formation
Retention
Drainage
Orientation
Two-sidedness
MD&CD profiles



Suitable wrap angle of forming roll

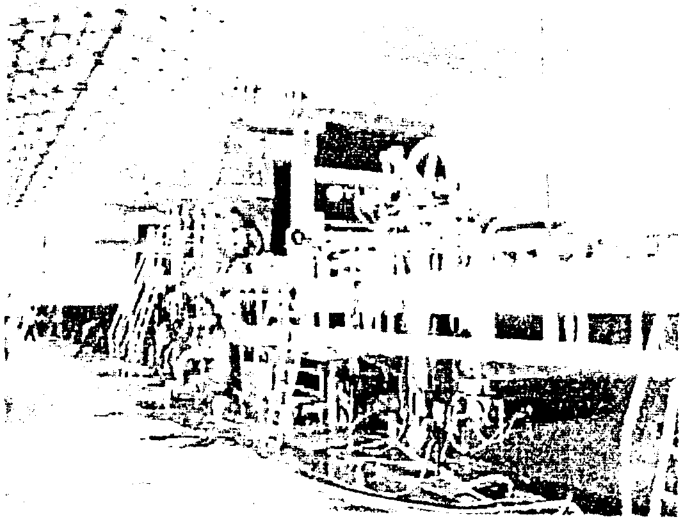
Loadable blades near the forming roll to achieve good formation

Source: Metso Paper

Wire sections of Indian paper industry

Old technology in wire section increases cost of papermaking. Filler content must be low and long fibre content high. Paper formation is not best possible and there are easily pinholes in the paper. Reduction of basis weight is difficult.

- **Headbox** technology is old: open headboxes, rectifier rolls, no automatic CD profile control.
- **Wire section** is normally Fourdrinier with dandy roll. Board machines are still mainly cylinder vat machines. Several machines are without suction pick-up. Even metal wires are used.
- There are only **few twin wire** machines. Even the newest machines can have machine size and technology from 1970s.
- With Fourdrinier and dandy roll it is impossible to get **high filler content** because filler is enriched to the top side. This increases dusting and reduces dry and wet pick. Also two-sidedness and curl of Fourdrinier paper are big problems.
- Low speed Fourdrinier paper is not highly oriented (tensile ratio 1.5 – 2.5). Paper made with a high speed gap former can have tensile ratios from 3 to 4. A **high tensile ratio** improves runnability and gives opportunities to reduce long fibre and to increase filler content



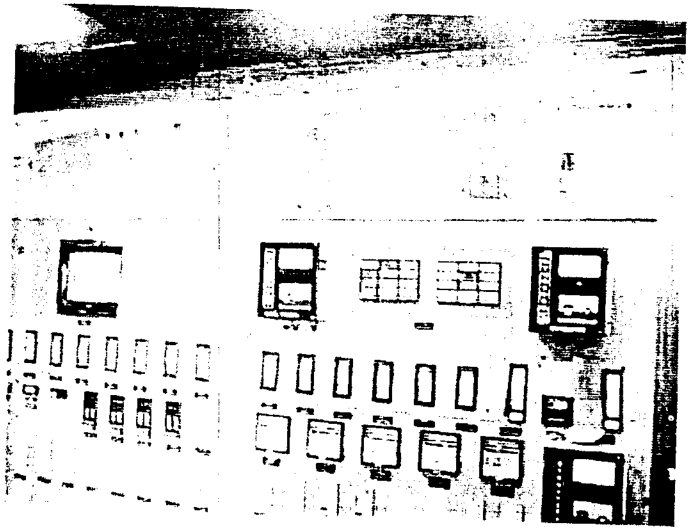
JAAKKO PÖYRY
Jaakko Pöyry Consulting

Improvement of paper quality

Domestic raw material quality & availability (fibres, pigments and chemicals) must be improved. Level of quality control systems and automation should be better.

- The level of **quality measurement and control** should be better. Cost of automation for a small machine is almost same as for a big machine. Bigger machines can afford better quality control systems (QCS and DCS).
- Classification of products and mills should be based on the customer **requirements** and their **converting processes**. Now the thinking is based too much on raw materials and mill size.

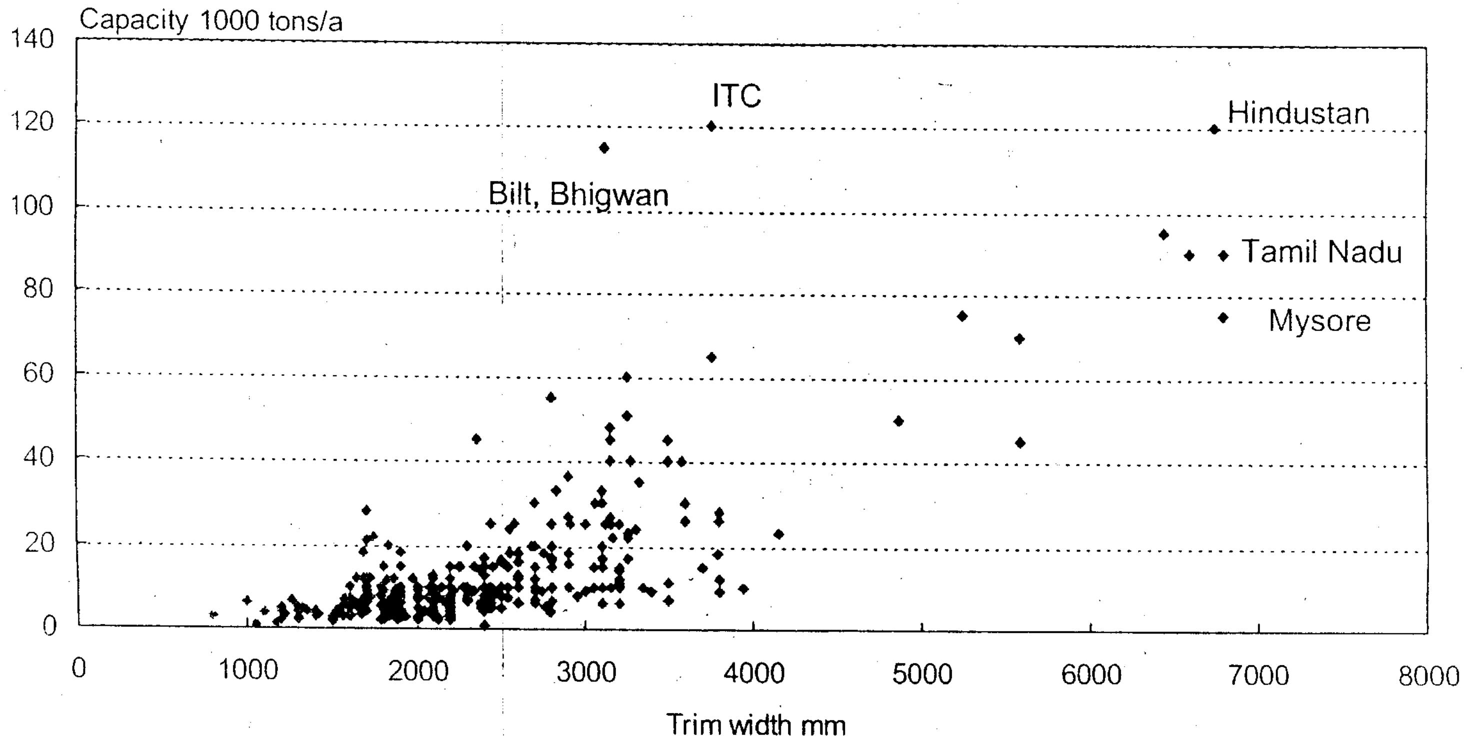
- **Bleaching** sequences should be improved to get the standard ISO-brightness of 89 %.
- **Mills must have export** to be able to improve quality and to meet the international competition and development.
- Indian paper industry needs more **international contacts**, joint ventures, training and applications instead of 100% Indian owned companies and own R&D. Input to **R&D** should be totally (mills and CPPRI) about **1% of turnover.**
- **Internet and mobile connections** from all mills should be working.



Paper machines in India 2002

Project Number 52A0087
Final Report

Most Indian paper machines have a trim width less than 3 metres

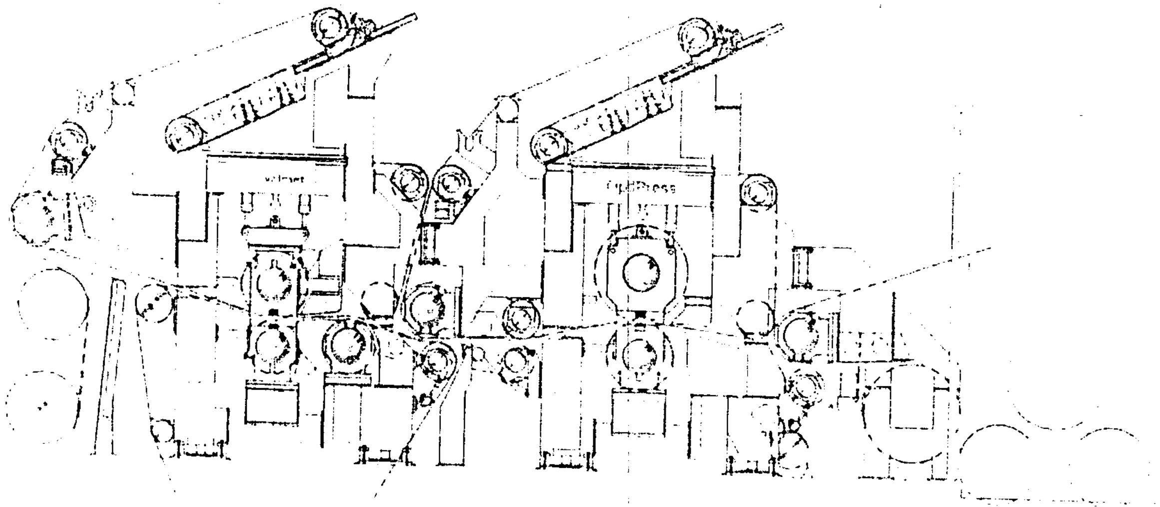


Better runnability with shoe presses

A two-nip press section with one or two shoe presses is today a standard solution for all paper and board grades. For Indian slow machines only one shoe nip might be best technology.

OptiPress

Roll Press and Shoe Press with Transfer Belt



Source: Metso Paper

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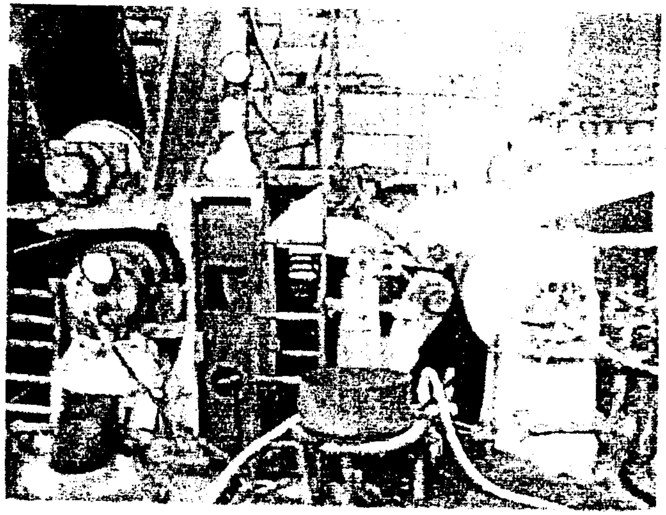
Press sections of Indian paper industry

Project Number 52A0087
Final Report

Open draws in press section increase cost of papermaking. Filler content must be low and long fibre content high. Solids content after press section in India is 5-10 %-unit lower than in developed countries. This increases steam consumption 25 – 45 %.

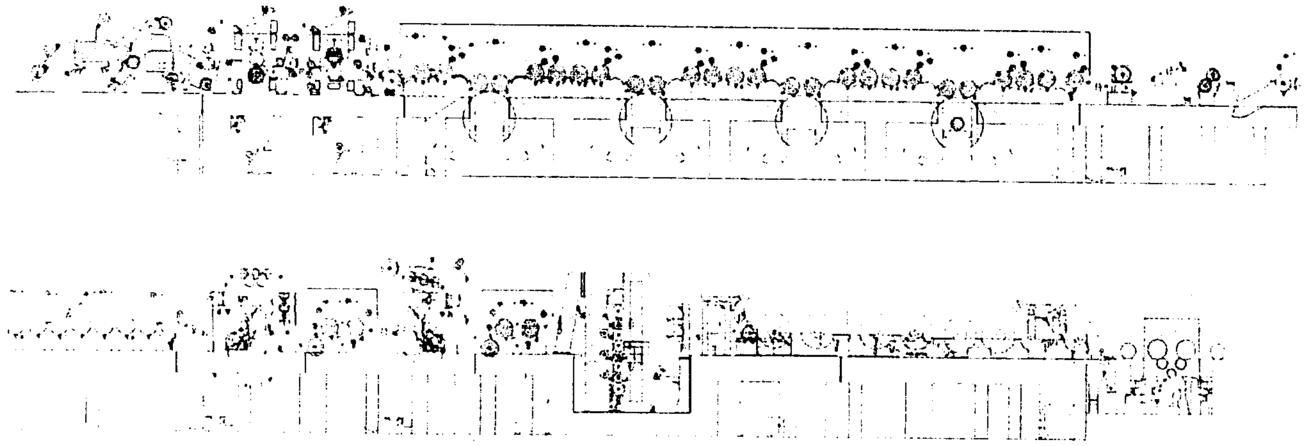
- Even if there is suction pick-up, open draw follows after first or second nip. Presses are usually pneumatically loaded with **very low linear loads**.
- A good press section is more important in India than in other countries because **fibres are short**. Initial wet web strength with Indian fibres is extremely low and would require best possible press sections.
- A good runnability in the press section allows **higher filler contents**. A higher filler content improves solids content and **reduces steam consumption** in the drying section.
- Indian agro fibres have very high water retention value. These fibres require time to dewater. Extended nip is the only good solution. A high speed machine with one-nip shoe press (or maximum two nips) would be the most suitable concept for Indian raw materials.



New drying concepts

Project Number 52A00857
Final Report

New drying concepts include web supported run with vacuum pick-up to dryer section and single-tier dryers. Hood is closed and there are efficient air and infra red dryers.



Source: Metso Paper

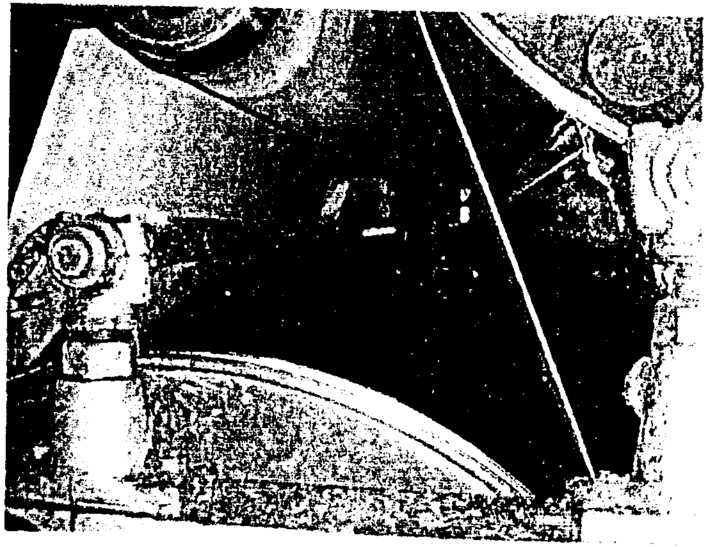
New drying concepts

Online coating

Online calendering

Drying sections of Indian paper industry

Unsupported web run is normal in Indian dryer section. Hood is open and steam consumption is high. Humidity profiles are poor, paper roughness is high and CD-profiles uneven. Moisture content of final paper is low and calendering very hard.



Web run in India is normally **unsupported**. This is OK when speed is low. When speed is higher than 600 m/min there should be some single tier dryer groups to avoid web flutter and breaks.

Hood in India is usually open. The **open hood** means that web is dry at the edges and moisture profile in the cross machine direction is poor.

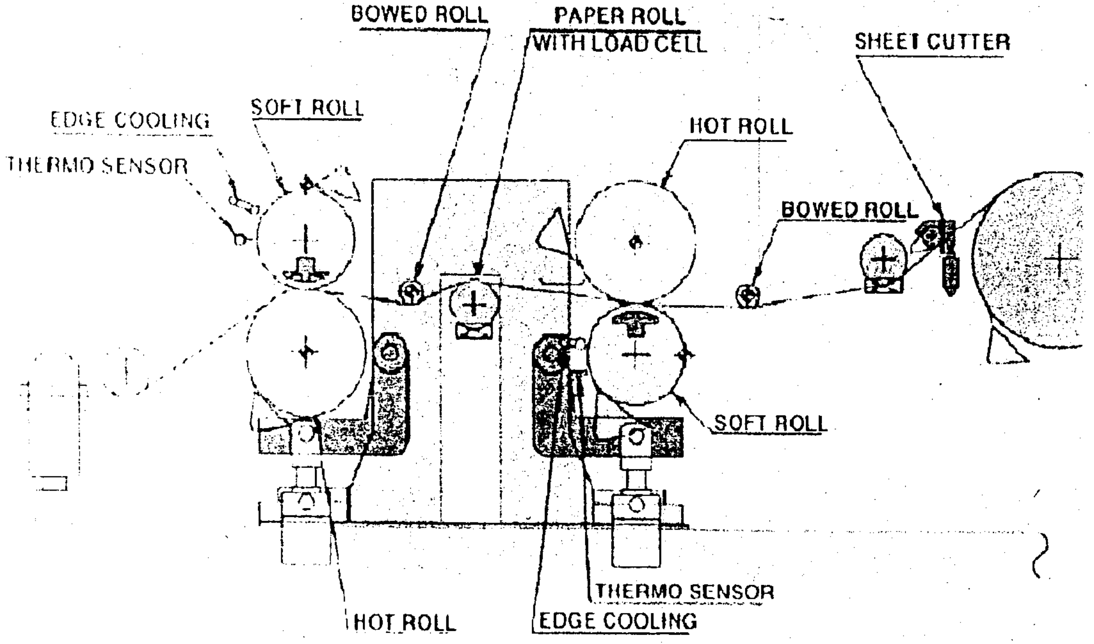
- To avoid calender blackening with uneven CD profiles the average moisture must be low. This increases paper roughness and decreases strength properties in the calendering. Web is dusty, **fibre rising** and roughening in the web offset printing is very high.

- In many cases there is **no on-line measurement of web moisture** at reel. Before size press the moisture measurement is uncommon. There are only few automatic CD-controls for moisture in India.

World class calendering technology

Project Number 52A0087
Final Report

For newsprint and woodfree papers state-of-the-art calendering technology is soft calendering or multinip calendering with soft rolls. Two stacks are normally not needed today. There are normally 2 - 6 rolls in the stack.

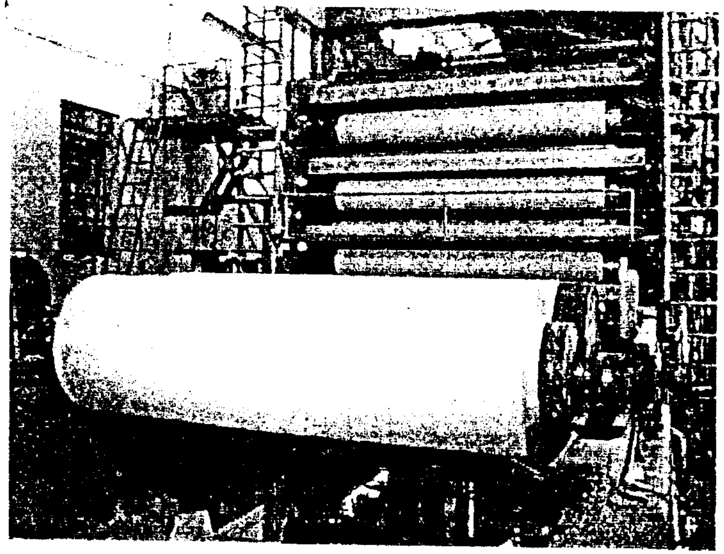


Calendering technology in Indian paper mills

Project Number 52A0087
· Final Report

Soft calenders are highly recommended to Indian paper industry. However, these require good CD-profiles and more investments in the process line.

- Indian calenders are normally **hard nip** calenders with four or more rolls.
- Soft calenders could **save bulk** and improve opacity, strength and smoothness. These are critical properties of Indian papers.
- However, soft calenders require **good CD profiles** because the possibilities to control caliper profile are not as good as with a hard nip calender.
- To improve the situation it is not enough to install a soft calender, but there should be a comprehensive **study of CD-profiles**. According to this kind of study it would be easier to consider the required investments with a new calender. This would be a key research area for CPPRI in the future.



Global Competitiveness of Indian Paper Industry : Constraints

High cost of transportation and power

Low scale of operation

Inferior pulp & paper quality

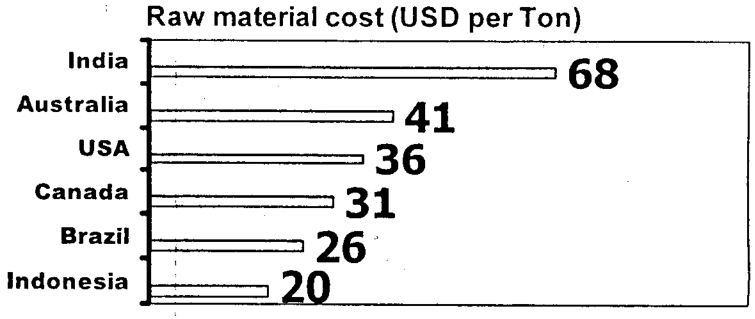
Low capacity utilisation

State of art equipment & machineries

High capital costs

High costs of raw materials

Only 20% of the total used paper is recycled in India compared to a global recycling average of 40%


Raw material cost (USD per Ton)

Key factors that will affect growth of Indian Paper Industry

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SIZING

INTERNAL SIZING (ACID, ALKALINE/REACTIVE, AND NEUTRAL)

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INTERNAL SIZING (ACID, ALKALINE/REACTIVE, AND NEUTRAL)

Y. V. Sood

1.0 INTRODUCTION

Of the different wet end chemicals used in papermaking, sizing chemicals are among the most frequently applied wet end additives. The usual objective of sizing is to impart aqueous liquid resistance to give cellulose product some desirable end use characteristics. Product, which are made resistance to liquid penetration are said to be sized. Thus sizing can be defined as a process by which a chemical additive provides paper and paperboard with resistance to liquid wetting, penetration and absorption.

2.0 REASON FOR SIZING PAPER

Papermaking fibers have a strong natural tendency to interact with water. This property is important to the development of strong inter fiber hydrogen bonds during papermaking. The behavior is an advantage for certain absorbent grades but such properties are not common for most of paper grades. **Table-1** lists some common examples where liquids penetration resistance is necessary.

TABLE-1

PAPER END USE AND CONVERTING REQUIREMENTS NEEDING LIQUID PENETRATION RESISTANCE

1. Liquid packing
2. Offset printing
3. Wet/Frozen foods packing
4. Water based ink holdouts
5. Off machine coating

Besides end use, liquid penetration resistance is also important to many papermaking processes where paper is brought into contact with aqueous solutions such as size pressing, coating etc.

3.0 TYPES OF SIZING PROCESSES

There are two types of sizing processes. One is surface sizing where the paper web is formed and dried and sizing agent is applied to the paper surface by a size press, coats or calendar box. Second is internal sizing where sizing additives are added to the papermaking furnish and get incorporated into the web when it is formed. Both processes offset the wetability of paper fibers, while surface sizing can also reduce the web pore size. The present discussion is mainly focus on internal sizing.

4.0 SIZING TERMINOLOGY

Before further discussion, it is right to discuss some terms that are frequently used in sizing. The term 'resistance" with respect to sizing is the characteristics that slow down or resists the passage of liquids through paper i.e. sizing is the rate phenomenon. The resistance properties are different from barrier properties. Barrier properties are attributes that absolutely prevent the passage of liquids through paper. Internal sizing produces resistance properties while other processes such as coating, saturation, or lamination are required to achieve barrier properties.

Paper are said to be waterleaf, slacked sized or hard sized depending upon their degree of sizing. These terms may be defined as follows.

Waterleaf papers: Very absorbent papers, which have no water resistance. (e.g. toweling tissues, corrugating medium)

Slacked sized papers*:* Paper that have intermediate levels of water resistance. (e.g. offset printing papers, writing papers)

Hard sized papers: Very highly sized papers that have high liquid penetration resistance (e.g. cup stock, milk carton raw stock)

Fugitive sizing: The disappearance of liquid penetration resistance in a paper that exhibits this property shortly after it is manufactured (e.g. a loss of more than 25% of the original sizing test value within seven days of manufacture)

Self sizing*:* The gradual development of water resistance in paper that does not have this property immediately after being manufactured. This phenomenon can occur by the vapor phase redistribution of naturally occurring resins and fatty acids.

5.0 BASIC SURFACE SCIENCE CONSIDERATION IMPORTANT TO SIZING

It has been hypothesized that liquid moves through paper by the following four mechanisms. [1]

- Capillary action through pores
- Diffusion through pores
- Diffusion through fiber solid fraction
- Vapor phase diffusion, evaporation and condensation.

5.1 Capillary flow in pores

Relationship between Contact angle and surface wetting:

Out of the four mechanisms listed above, the most attention has been paid to capillary flow in pores. Wash burn equation was developed to describe the penetration of liquid into fiber beds.[2]

$$\frac{dl}{dt}=\frac{\gamma \cos \theta . r}{4 \eta l}$$

where ,

.l=Capillary distance penetrated in time t
r=Capillary radius
η =Liquid viscosity
θ = Contact angle between capillary walls & liquids
γ =Liquid surface tension

From WashBurn equation, it is clear that in order to achieve low capillary penetration, it is necessary to have a high contact angle and/or a small capillary radius. Applying film-forming substances at the size press can reduce paper pore radius. The contact angle is influenced by several factors. When a non-volatile pure liquid drop is placed on the clean, smooth, insoluble surface, a balance of forces is established between the liquid and the surface. If the forces between liquid and solid are greater than forces between the molecules within the liquid, then the drop will spontaneously spread on the solid surface. This is referred to as wetting behaviors. If forces reach an intermediate balance, then the liquid drop will establish the contact angle with the solid **(Fig.-1).** When the contact angle is less than 90^0 , the liquid is said to wet the surface. When the contact angle is greater than 90^0, no wetting is said to occur **(Fig.-2).**

The second equation is Young's equation, which gives the relationship between contact angle and surface tension. A balance of forces existing at the line of contact between the liquid and solid in above figure is expressed by the Young's Equation,

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$$

The above two equations i.e. Washburn and Young equation provide a way how internal sizing acts to impart water resistance to paper. Sizing agents are hydrophobic and lower the surface energy (surface tension) of the fiber surface (γ_{SV}), thereby reducing the value of numerator in Young's equation. As (γ_{SV}-γ_{SL}) decreases, $\cos\theta$ decreases also and dl/dt in Washburn equation becomes smaller. Thus a water penetration decreases the objective of internal sizing. In the extreme hard sizing becomes less than zero and capillary repeats the penetrating liquid.

6.0 REQUIREMENT OF GOOD INTERNAL SIZING AGENT

Since sizing is the process where a sizing agent is applied to papermaking fiber to lower their attraction for liquid water, a sizing agent must have the following properties.

- Have high retention on fibers
- Be uniformly distributed on fiber surfaces
- Be able to produce hydrophobic fiber surfaces
- Adhere strongly to fibers
- Be chemically inert to the penetrates of interest like surface sizing chemicals, coating chemicals etc.
- Should not have any adverse effect on the papermaking process

7.0 COMMERCIAL SIZING AGENTS

The predominant types of sizing agents currently used all over the world rosin based, wax based and cellulose reactive materials. Rosin based sizing agents are still most widely used in our country.

7.1 Forms of rosin used in papermaking

Rosin is naturally occurring solids, resinous material obtained from pine tree. It is used in paper making process in two forms. Neutral size (sodium rosinate) and acid size (rosin acid).

7.1.1 Neutral rosin

Three forms of neutral rosin are currently available to paper makers

1. An 80 % saponified product generally marketed as 70-80% solids fluid. This product is normally manufactured by reacting rosin acid with sodium carbonate.
2. A fully saponified product marketed as 100 % solid power. This material is readily soluble in water. This material is readily soluble in water. They are prepared by spray drying or drum drying a fully

saponified high solid paste. It is normally used by paper mills located far from a size manufacturing facilities, where transportation cost is a major factor.

3. A 50 % solids containing system that contains a 50:50 mixture of neutralized rosin and urea and urea known as their size, which can be readily transported, pumped and diluted for use in stock.

7.1.2 Rosin acids

Rosin acids are available in a variety of emulsion having 75 to 90 % free rosin content. High free rosin size emulsions are milk white liquids, commonly containing 40 to 45 % total solids. Particle size varies from 0.5 to 5 µm, but for best efficiency should be in the range of 0.5 to 1 µm.

7.1.3 Modified Rosin Size (Or Fortified Rosin Size)

As a result of extensive experiment with rosin sizes, it was discovered that rosin sizing efficiency could be markedly improved by reacting the levopimaric acid component of rosin with maleic anhydride, fumaric acid, itaconic acid or other acids that could undergo a Diels-Alder reaction with the material. The reaction product contains three carbonyl groups and is more hydrophilic and anionic than original levopimaric acid.[3]. The fortified rosin products leads to improved performance either due to the extra carbonyl groups which provides more reaction sites for alum and hence promote stronger anchoring of size molecules of fibers surface or being more anionic they tend to form smaller particle size and their by distributed over the fiber surfaces more widely and uniformly [4].

8.0 ROSIN SIZE SELECTION

The relative effectiveness of different rosins, rosin modifications and sizes varies with type of pulp, waters pH, total acidity, drying and type of machine. However, there are some rules of thumb useful for general consideration.

8.1 Dark v/s pale rosin

Less of brightness caused by dark size precludes its use in high brightness pulp (Dark size can be use up to 50 to 60 brightness). Dark sizes are less expensive than pale and therefore normally used in unbleached grade.

8.2 Fortified v/s non fortified size

In bleached pulp, fortified size usually offer more sizing per kg than non fortified size and this difference increases with increasing brightness of pulp. The pH of the system also effects the selection. At higher pH, fortified size gives less advantage. In few mechanical pulps, fortified size dies not proved economical as compared to non fortified size and also in pulps, which are difficult to size, the fortified size is less efficient.

8.3 High free rosin v/s saponified size

The use of high free rosin size emulsion are found to be more efficient where process water hardness is more. Pulps, which are very hard to size, are sized effectively by size emulsion. The wastepaper furnish containing calcium carbonate filler sized effectively by size emulsions.

9.0 DIFFERENT ALUMINUM COMPOUNDS USED IN PAPERMAKING

Alum is still most widely used aluminum compound. The second compound was sodium aluminates. Recently, poly aluminum chloride is gaining importance as a source of aluminum in papermaking due to its high cationic charge. Aluminum chloride has been used in specialty technical paper grades where the sulphate ion is considered undesirable. Here we are discussing the first three compounds in brief.

9.1 Alum

The alum or "papermaker's alum' as commonly termed is still the most excessively used aluminum compound in paper making. Some typical properties of alum is summarized in ***Table 3.*** [5]

TABLE- 3

TYPICAL PROPERTIES OF COMMERCIAL ALUM

Property	Dry	Liquid
Chemical formula	$Al_2(SO_4)_3\ 14H_2O$	48.5% soution
Molecular weight	594	-
Al_2O_3 equivalent	17.1	8.3
Bulk density, ground (kg/m^3)	1000-1100	-
Specific gravity (@ 15.5 ^oC		1.335
Density (kg/m^3)		1330

Kg alum/m^3	647

9.2 Use of alum in papermaking

The role of alum in papermaking is multifold. Besides sizing additives it is als benefitial for other purposes. Below are some uses of alum in papermaking.

- Rosin sizing agent
- pH control agent
- Retention aid (dyes, filller, fiber fines)
- Drainage aid
- Formation aid
- Anionic fresh charge neutralizer
- Water purifying coagulant
- Pitch control agent
- Alkaline papermaking contaminant scavenges
- Acid catalyst for wet strength rosin cure

In addition to the advantages gained from alum use listed above, there are also several notable disadvantages associated with alum. These are listed below:

- Alum based systems, being acidic are corrosive
- Alum can degrade paper strength when used in excess
- Alum-containing papers are impermanent
- $CaCO_3$ fillers can not be easily used with alum furnishes
- Alum deposits can be a serious problem in the wet end of a paper machine.

9.3 Sodium Aluminate

Sodium aluminate is used in sizing process as a source of alumina. Some features of sodium aluminate are

- Easier and safer to handle than caustic
- Contains no sulfate ions whereas liquid alum contains about 48% sulfate ions
- Eliminate Barium sulphate and other metal cations deposits
- It is nearly iron free
- Addition of alum and caustic at some addition pint would create deposits, $NaAlO_2$ can be used at such place.

6.3 Polyaluminium Chloride (PAC)

PAC refers to a series of polyhydroxide chlorides of aluminum with the general formula $(Al_n(OH)_{3n-m}$, whereas m determines the degree of neutralization, with hydroxyl ions substituted for part of the chloride ions of aluminum chloride. The degree of polymerization in PAC is characterized by the % basicity which is defined as % basicity = 100 x $(OH^-)/(3[Al^{+3}])$ where (OH) and (Al^{+3}) are the molar concentration of hydroxide and aluminum ions, respectively [6,7]. PAC's used in papermaking typically have basicities of 25-75%.

The effectiveness of PAC is strongly dependent on how it is manufactured and basicity. PAC can be synthesized by many ways.

- Treating aluminum chloride with a base, such as NaOH, Na_2CO_3, NH_4OH or lime.
- Reacting aluminum hydroxide with HCl
- Dissolving aluminum metal in aluminum chloride.

PAC's have been used for a variety of papermaking applications such as sizing (dispersed sizes under both acid and alkaline pH conditions), pitch control, white pitch control, deposit reduction, fines and filler retention and interfering substance neutralization (acid and alkaline papermaking systems).

7.0 MECHANISMS OF SIZING FOR ROSIN SOAP SIZE AND DISPERSED ROSIN SIZES

7.1 Rosin soap size

The rosin soap size must meet the following requirements to be a good size

1. The rosin precipitate must be retained well on the fibre surfaces and be uniformly distributed.
2. The retained rosin must have a low energy and therefore a higher hydrophobicity.
3. The wet rosin precipitate must be transformed to a stable low energy surface, which remains unchanged when brought into contact with water.

Rosin soap size meets the above requirement by the following mechanism [8,9]

1. The neutralized rosin acid reacts with alum in the stock preparation system and on the paper machine wet end to form a positively

charged alum rosin precipitate that is attached to the negatively charged fibre surface and is retained there.

2. The aluminum, rosin and fibre react in the dryer section to form a stable size complex that is attached to the fibre surface (**Fig 3**) illustrates this mechanism schematically.

The most efficient sizing occurs with rosin soap in pH ranges 4.5 to 4.8 where alum exists primarily in the Al^{+3} and hydroxyaluminum complex forms. The formation of aluminum resinate occurs by reactions between neutralized rosin molecules and these aluminums species.

7.2 Dispersed Rosin Sizes

The machines, which dispersed size meets the requirements of a good size differs from soap size in several important aspects. First, the retention of depressed rosin size by fibres is only lightly aided by alum. Cationic starch, or synthetic cationic polymers are used to promote the retention of anionic dispersed size. While cationic dispersed size is essentially self-retaining.

The retained dispersed size particles on fibre surface when reaches the dryer section, melts (sinter) and spread out on the fibre surface, where they come into contact with aluminum species and retention occurs that bond the rosin to the fibre surface. This process is promoted by the lower melting point of dispersed sizes (70-110°C) compared to soap sizes. **Fig 4** showed the schematic illustration of entire mechanism.

8.0 MILL FACTORS THAT INFLUENCES THE SIZING

The addition of size and alum to paper stock does not guarantee that the finished sheet of paper will be well sized. There are many mill factors, which influence the sizing. The major paper properties that determine degree of sizing are:

- Contact angle between the paper surface and a drop of the test liquid.
- The mechanical structure of the sheet (pore radius)

The various mill factors discussed in ***Table 4*** modify either one or both of these properties.

TABLE - 4
MILL FACTORS THAT AFFECT SIZING

Factor	Sizing effect
Stock Temperature	High stock temperature reduces the effective charge of aluminum species thereby reducing sizing.
Effect of anions	Presence of high amount of $SO4^{-2}$ citrate, hexamate, phosphate ion level in mill system retards sizing.
Process water quality	High Ca^{++} content in hard water reacts with soap size to produce a calcium and magnesium resinate precipitate that does not produce sizing.
Pulp Type	Highly bleached or purified pulps are difficult to sized than unbleached pulp. Kraft or sulphate pulps are easy to size than sulphite pulp. Dispersed rosin size is less affected by pulp type than rosin soap size.
Refining	Refining increases the amount of size needed. Also release hemicelluloses and other anionic materials that react in alum and reduces its availability to react with size.
Effect of fillers	With an increase in the filler content of paper demand of sizing chemical increases e.g. clay.Talc does not give much change in sizing demand. $CaCO_3$ filler has most pronounced effect on sizing.
Effect of starch	Generally starch has no effect on rosin sizing, but the alum consumption goes up.
Effect of drying condition	Proper sizing with rosin soap/dispersed rosin sizes can be obtained only when proper sintering temperature is reached at dryer section.
Effect of cylindering	Higher moisture content of paper, results in greater sizing loss at calendering (5-6% moisture shows 40 to 50% sizing loss at calender.

9.0 CELLULOSE-REACTIVE SIZES

With the advent of technology in last decades, introduction of several synthetic sizing agents take place that react chemically with the hydroxyl groups of cellulose fibers. They can produce permanently anchored monomolecular layers of hydrophobic material on fiber. Although much expensive than rosin, they are superior on cost effective basis. Since they perform most efficiently in neutral to alkaline paper making systems, the paper machine can be operated at higher pH and is advantageous in better paper permeance, reduce machinery corrosion and increased paper strength resulting from increase swelling at higher pH. Out of the number of synthetic organic molecules capable of imparting water resistance to paper, only AKD and ASA have been widely adopted by paper industry.

9.1 Alkyl Ketene Dimer (AKD)

AKD is the most commonly used of the cellulose reactive sizes in paper industry. The molecular structure is shown in **Fig 5** where R represents a hydrocarbon chain having 14-16 C atoms.[10]. The 4 membered ketene dimer lactone rings provides AKD with a functional group that reacts with cellulose hydronyl groups to form anester linkage. The lengthy hydrocarbon chains on these amphipatic molecules contribute excellent hydrophobicity to the fiber surface. AKD is generally manufactured from a mixture of palmatic and stearic acid. Ketene formation and dimerization is carried out with the fatty acid chloride derivatives in an organic solvent. The low melting (40-50°C) AKD product is then melted and emulsified in water containing cationic starch and commercial surfactant in order to produce a stable AKD particle suspension at room temperature. The particle size is 0.1-1.0 µm with 6-15% AKD solids. The diluted AKD suspension is added to pulp slurry, close to fan pump, together with cationic starch to serve as the size retention aid.

9.1.1 Mechanism of sizing with AKD

The AKD size is generally used at a pH of 7-9 in bleached kraft systems. They are especially useful in sizing pulp slurry containing $CaCO_3$ filler. Alum is not required in AKD sizing process. (**Fig 6)** The low melting point of AKD allows it to spread very readily over the surface of cellulose fibres during elevated temperature drying of the sized paper; good distribution and proper orientation of the AKD molecules then leads to reaction with the cellulose substrate. The AKD addition level is quite low to produce desired degree of water repellence for the paper product. The strong covalent bond of AKD proved a good resistance to acidic and alkaline penetrates. AKD sized paper retains much of its original brightness and strength, as comparison to sized at low pH in rosin alum system.

9.2 Alkenyl Succinic Anhydride (ASA)

ASA is the other popular synthetic size in alkaline papermaking. ASA is preferred in several applications because its greater reactivity (higher on machine sizing) and better size press hold out. It is mostly preferred in fine papers. It is synthesized in two-stage process. Firstly the random isomerization of the double bond position inan alpha-olefin and then the internal olefin is reacted with malic anhydride to form the final product. The ASA product is a yellow to amber liquid at room temperature.

9.2.1 Mechanism of sizing with ASA

ASA reacts with fibers to form ester bonds with accessible cellulose and hemicelluloses hydroxyl groups. These lineages enable the molecules to orient its hydrocarbon side chains out from the sheet surface and import a hydrophobic nature to it. (**Fig 7**) However, ASA reacts readily with water. Due to rapid hydrolysis may also reduce the sizing efficiency of ASA in hot stock system. The hydrolysis product is a modified fatty acid that would perform as an anti sizing agent under concerted into aluminum salt from so alum addition is generally recommended to minimize this adverse effect.

10.0 MEASUREMENT OF DEGREE OF SIZING

There are a wide variety of sizing tests employed by the paper industry. ***Table 5*** lists several of most common tests. Most size testing methods falls into one of two categories. In one groups of tests the amount of water that a paper specimen can absorb in a given time period is measured. In the other group of tests the time required for water to penetrate through a papers specimen is determined. Few tests, such as the pen and ink and contact angle tests, do not fall into these two classifications.

Since liquids can penetrate paper by a variety of mechanism, and different size tests emphasize are mechanism ones another, the retention of an appropriate size tests is difficult. The best way to select the test being tested. Before discussing the test methods let's have a look on various factors that affect sizing test.

11.0 FACTORS AFFECTING TESTING

There are number of factors that affect the role of penetration of aqueous liquids into paper or paper board independent of the degree of sizing of the paper. The most important are as follows.

- Temperature of sample, testing liquid and atmosphere in which test is conducted.
- Moisture content of sample.
- Pressure of liquid against the sample.
- Composition of testing liquid.
- Preparation of sample, including wrinkling, creasing, soiling etc.

TABLE- 5

SIZE TESTING METHODS

Name of test	**Property measured**	**Type of paper and board**
Water drop absorption	Time required for droplet of water to be absorbed by paper.	Heavy paper and paperboard, tissues, toweling.
Ink flotation test	Time required for writing ink to penetrate through a floating specimen and change the colour of the upper surface.	Moderately sized paper
Hercules photo size test	Decrease in reflectance of the opposite side of a sheet of paper which has been covered with a given amount of ink	Wide range of sized papers
Cobb size test	Amount of water absorbed by a given area of paper in specified period of time	Paper and papers boards that do not become saturated too quickly.
Pen and ink feathering test	Extent of spreading of lines drawn on sample with a steel pen and ink.	Bonds and other writing paper
Contact angle	Tangential angle from the horizontal which the base of a drop of liquid develops when carefully placed on a sheet of paper	Any paper of beard that does not absorb the drop too quickly for the measurement to be made
Edge penetration test edge witching test	Lineal penetration of liquid in the in-plane dimension of paper.	Extruded papers, et. Liquid packaging, photographic

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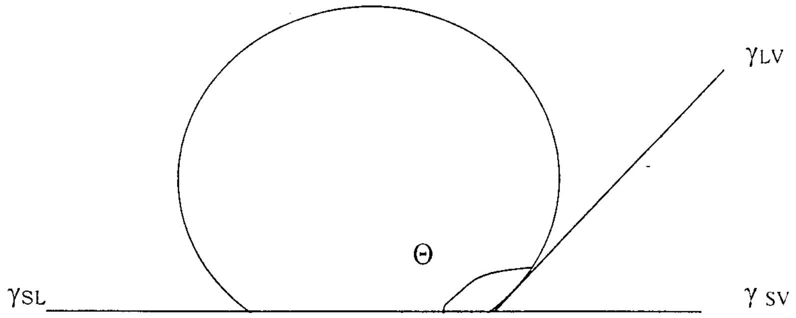
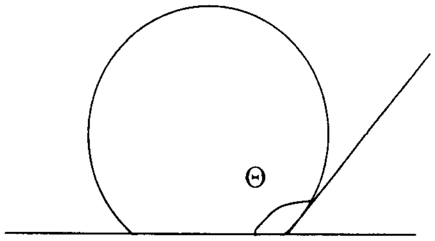
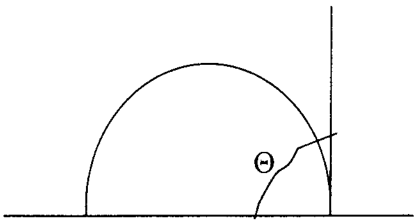


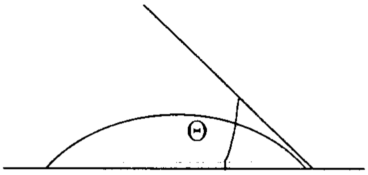
FIG 1: CONTACT ANGLE BETWEEN A LIQUID DROP AND SOLID SURFACE



Θ >> 90 degrees



Θ = 90 degrees



Θ << 90 degrees

FIG 2: RELATIONSHIP BETWEEN CONTACT ANGLE AND WETTING

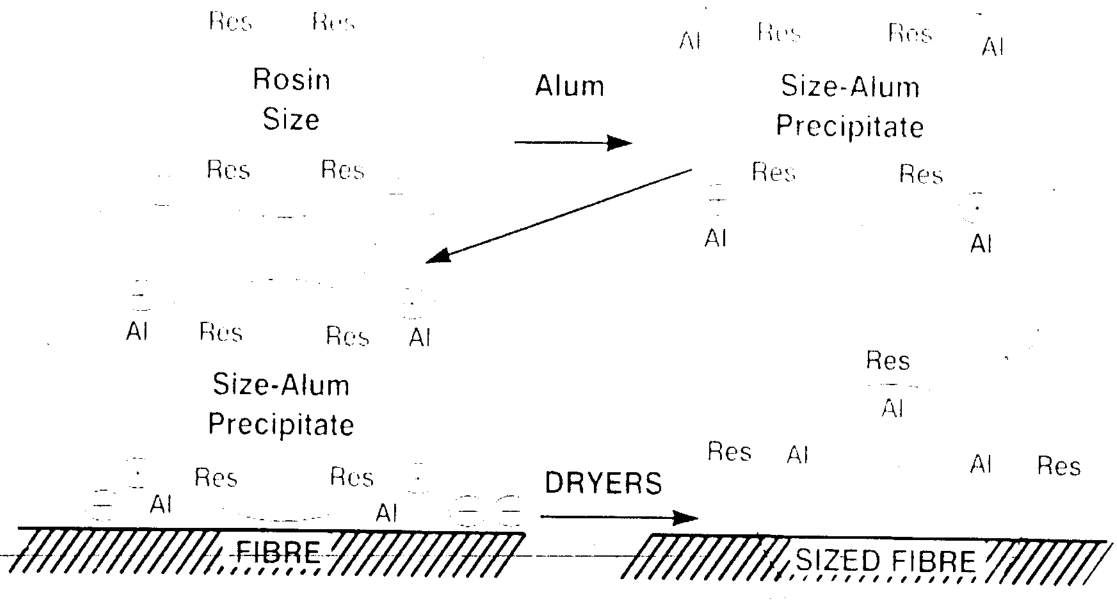


FIG 3: MECHANISM OF SIZING WITH ROSIN SOAP/ALUM

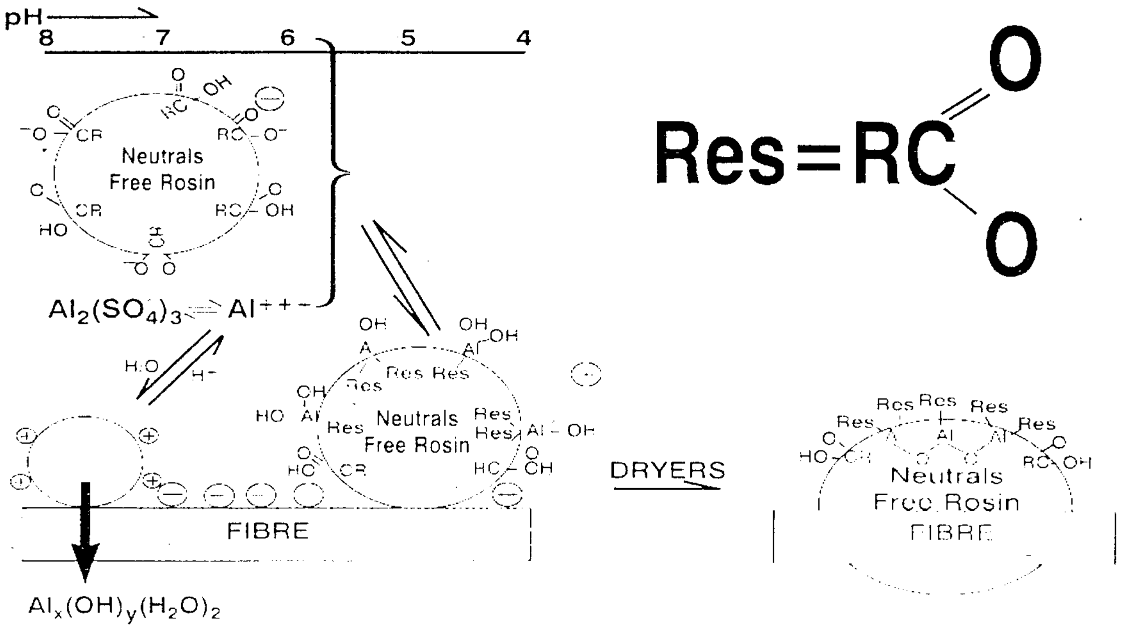
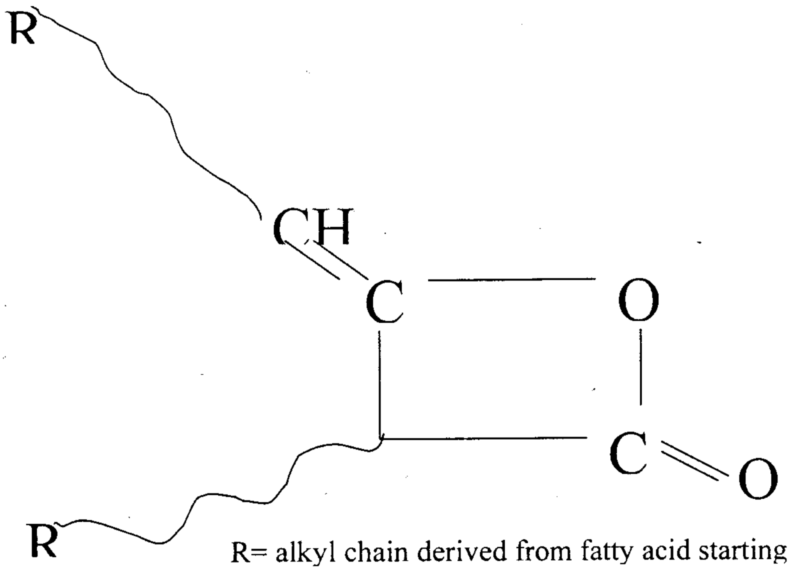


FIG 4: MECHANISM OF SIZING WITH DISPERSED ROSIN/PAC OR ALUM



R= alkyl chain derived from fatty acid starting material

FIG 5: CHEMICAL STRUCTURE OF AKD SIZE

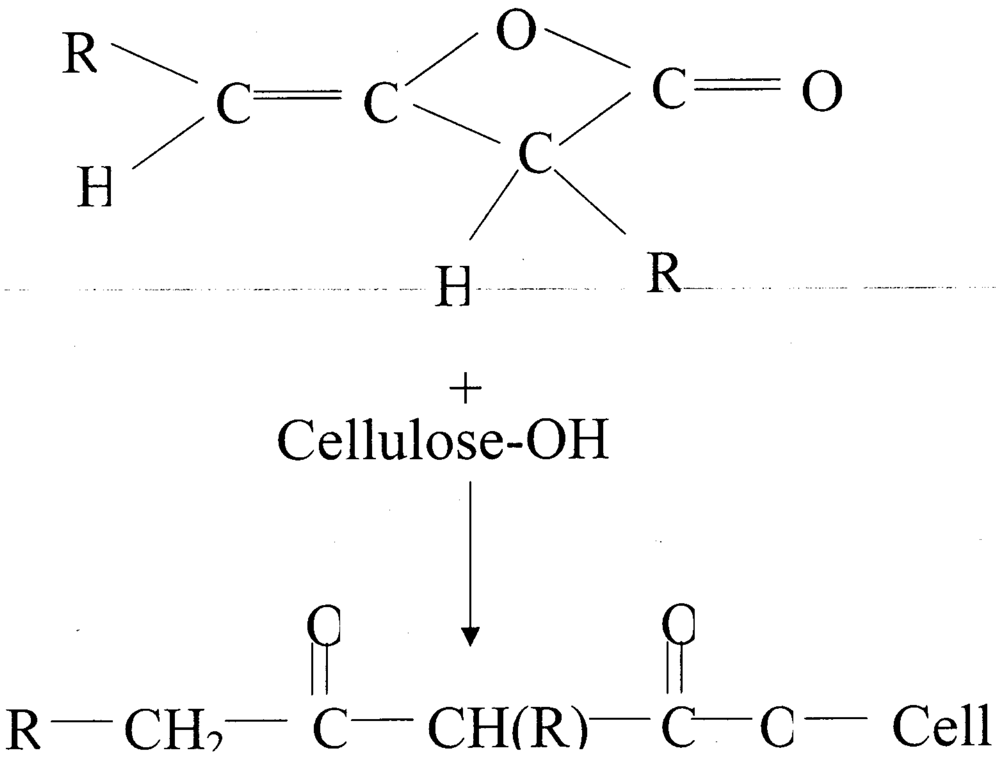


FIG 6: REACTION OF AKD WITH CELLULOSE HYDROXYL GROUP TO PRODUCE A KETO ESTER

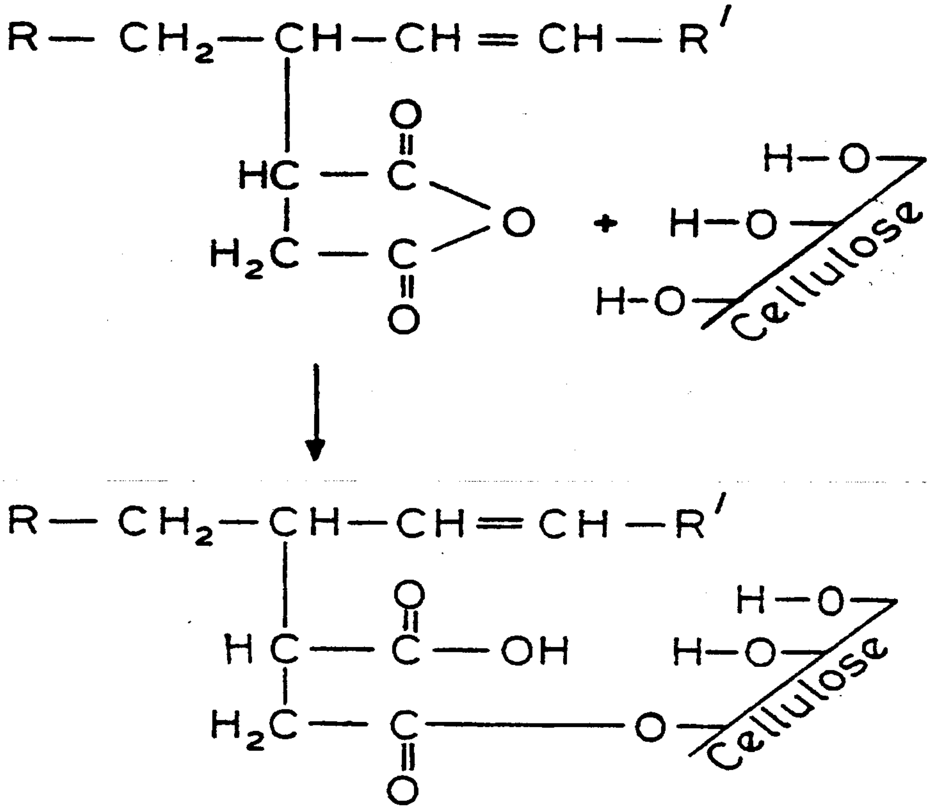


FIG 7: MECHANISM OF SIZING WITH ASA

SURFACE SIZING

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SURFACE SIZING

Sanjay Tyagi

1.0 INTRODUCTION

During the drying operation of paper, paper tends to take on the characteristics of the surface against which it is dried. These characteristics on the paper surface are not often desirable. Sometime other operations are applied which influence the surface characteristics of paper. Some of these operations are carried out on the paper machine while other are off machine. There are four surface modification methods. These are machine calendaring, supercalendering, surface sizing and coating.

Machine calendaring and supercalendering are the surface treatments where surface characteristics are altered by changing the nature of the surface fibers. Nothing is added or subtracted from the sheet. Surface sizing and coating on the other hand involve the addition of substance to the surface.

2.0 OBJECTIVE OF SURFACE SIZING

The two major objectives of surface sizing are:

- To bond the surface fibers or to increase the degree of surface fiber bonding, especially for the fibers or other elements (e.g. vessel elements) that are different to bond and thereby to pick out during printing.
- To increase the sheet's resistance to water penetration by filling in voids capillaries and small holes in paper.

3.0 SALIENT FEATURE OF SURFACE SIZING

- Surface sizing of a sheet of paper provide resistance to penetration of liquid by reducing pore radius.
- Surface sizing give better surface properties to the sheet.
- Surface sizing improves surface strength and internal bonding strength
- Surface sizing is a key element in making an improved base stock for coating.
- In comparison to internal sizing, surface sizing provides close to 100% retention of added chemicals - reduce problems of wet end deposition and increase life of machine clothing.
- Compare to wet end sizing, surface sizing allows reduction or removal of chemical from the white water to assist in environmental improvement.

4.0 SURFACE SIZING TECHNIQUES

In the conventional pond size press, the objective is to flood the entering nip with sizing solution; the paper absorbs some of the solution and balance is removed in nip.

Conventional pond size press configurations are generally categorized as vertical, horizontal or inclined as shown in ***Fig 1***. The vertical configuration provides the easiest sheet run, but the pond depth of solution in each nip is unequal. The horizontal size press arrangement solves the problem of unequal absorption by providing identical pond forms on either side of the sheet. The inclined size press is a compromise, developed to avoid the awkward vertical sheet run of the horizontal size press.

In the pond size press, the size penetrates deep into the sheet structure. Runnability is good at lower machine speeds but at speed above 800m/min, the pond size press is restricted due to runnability and pond splashing problems. The two-roll pond size press has been commonly used as a simple precoating technique for coated wood free papers.

5.0 MECHANISM OF SIZE TRANSFER PROCESS

Size transfer in pond size presses take place in three phases. In the first phase the size is absorbed into the paper in the pond. Then the paper web is compressed in the roll nip and size penetrates into the sheet structure. The third phase consists of the film split. In the film press unit, the lack of pond excludes the size absorption. The size transfer can be described by Young-Laplace equation

$$\Delta P = (2.\ \gamma_l \cos\theta).\ 1/r$$

where, ΔP=Pressure forcing size into pores

γ_l = surface tension in size solution

θ = Contact angle

r = pore radius

The mechanism of one sided film press process is shown in ***Fig 2***, where the entering of the transfer nip, the coating transfer and the final film split of bulk coating is present. The coating film in the nip immobilizes due to pressure dewatering and there by create an infinite viscosity. A transition area develops between the immobilized layer and the coating color with initial dry solids content most probably consists in the nip. It is strongly controlled by the base paper openness and color properties such as pigment shape and dry solid content. The coating film will split in the area with the lowest resistance in z- direction, which naturally is the area in the non-immobilized color with the lowest solids content.

6.0 TRANSFER PROCESS COMPONENTS

6.1 Roll cover and nip load

To ensure sufficient cross directional profiles, the size press always require a straight nip load. Nip load between 10kN/m to 40kN/m are required in film presses to maintain stable runnability and paper quality. In pond size press, the nip load dramatically affects the pickup. The nip load directly influence the specific pressure distribution in the nip and a harder roll cover increases the transfer. Linear load under 25kN/m are often used with cover softer than 25 P

& J, where nip slippage can cause tension and wrinkling related problems. One way to eliminate this problem is to use speed controlled drive for both the rolls instead of master drive roll. Hardness difference between the applicator rolls also causes slip in the nip, so rolls of equal hardness is used to achieve a static friction situation between the covers. This requires a straight take-off angle from the nip exit to make the web follow the most desirable roll surface. The roll cover is one of the most important transfer components in film press processes. The metering elements also put different requirements on the cover material. Grooved rods require non-abrasive and not too hard covers. Smooth rods demands for maximum hardness for good profile. Both polyurethane (PU) and rubber covers are used for all metering elements.

6.2 Base paper

To achieve an acceptable film coated paper quality, it is necessary to optimize the base paper qualities. The high fines content in the pulp tends to give denser sheet, which is necessary for sufficient coverage. The paper porosity plays an important role. The paper should be less "porous", to reduce the coating penetration in web. Lowering the freeness level, increasing the filler content or pre-caendering, can close the paper structure. Precalendering of base sheet improves the surface coverage and coat weight uniformity of coated paper due to homogeneous coating distribution. The topographical variation reduction takes place in precalendering which improves surface uniformity.

7.0 SPECIFIC RUNNABILITY PROBLEMS

7.1 Uneven size pickup

In the conventional size press, the size solution is delivered to the nip between a pair of oppositely rotating rolls to form a pond of material above the nip. With high speed roll rotation and high speed movement of web, the pond tends to absorb kinetic energy from the moving web and rolls. As shown in ***Fig 3***, an excess of liquid is flowing towards the nip, but the nip pressure of the roll limits the amount of sizing solution passing through the nip, causing the remaining solution to flow back upwards. If hydrodynamic force is too great, this upward velocity becomes high enough to cause the solution to break the surface of the pond and splash out of the nip. This pond turbulence and "nip-rejection" results in uneven pickup of solids across the machine.

Size solution viscosity contributes to the hydrodynamic force in the roll nip. As machine speed increases, it becomes necessary to dilute the solution, which in turn affect the drying capacity of the machine.

7.2 Film splitting

Another problem associated with size press is film splitting. Although most of the size solution is absorbed into the sheet at and after the nip, excess solution remains on the surface of the sheet between the paper and roll. At the exit of the nip, this film is split into two layers with part following the web of the paper and the rest remaining on the roll surface as shown in ***Fig. 4.*** This pattern will appear as heavy rings of fluid across the roll face. The severity of this pattern depends on the rheology of the size, absorption properties of the sheet, speed of the rolls and volume of material being split. The problem becomes worse at high speeds, higher viscosity and higher film thickness.

Moisture content of the sheet entering the size press has a significant effect on the pickup. Higher moisture content promotes moisture absorption thus a variable moisture content across the machine causes variation in pickup and sheet properties affected by surface sizing.

7.3 Transfer nip misting

When the coating film passes through the nip, it is generally accepted to split in the middle of non-immobilized layer due to a low z-directional resistance. At this point, the film split of an excess amount of non-immobilized coating causing a color mist at the web release. This phenomenon is termed as transfer nip misting. (***Fig. 5***). The color mist formation occurs in four steps in film splitting at forward roll nip. (i) Cavitations (ii) Filament Formation (iii) Filament elongation (iv) Filament rupture.

Misting phenomenon is an effect of centrifugal force throwing the excess of non-immobilized color from the roll surface. The color mist at the nip exit generally increases exponentially as the function of both the machine speed and coat weight.

The color misting can be reduced by

- Increasing the coating color solid contents.
- Reduce color viscosity.
- Reduce coat weight.
- Reduce amount of blocky pigment.

It can also be reduced by

- Increasing nip pressure
- Speed difference between the rolls
- Increased contact distance paper / coating.
- Harder roll cover.
- Lower speeds.

Increasing the basis weight of base paper, and porosity also reduced the misting phenomenon.

7.4 Coating color drying on roll surface

The trend towards an increased dry solids content has brought forward the sensitivity for coating colours to dry on the roll surface. This occurs when the coating film is completely immobilized from the paper to the roll surface. Then there is a lack of non-immobilized color available to give stable film split. The film split then takes place at the paper coating interface, and dry coating layer rapidly accumulates on the roll surface and becomes thicker for each roll revolution.

The build up of a dry coating layer on the roll can initially appears as streaks, which gradually develop into a thick layer. The main reasons for the coating color drying on roll surface are

- High solid content of the coating colours.
- Low machine speed
- Low water retention of the coating color.
- High content of platy pigment or soft polymer binder
- High linear nip pressure or roll hardness.
- High base paper and/or coating color temperature.

The dry streak or a dry coating film which gradually grows in thickness is dangerous to both rod and roll cover. The surface of coated paper is deteriorated depending upon the degree of build up. The friction between the roll cover and the rod increases dramatically, which can destroy the roll surface and create scratches in the rod. To avoid the roll and rod from being destroyed, the streaks or layer of dried color need to be immediately removed.

7.5 Web Release

The web release is critical in a film press process where both sides are coated simultaneously. An uncontrolled web release or web stealing, appears as a web fluffer between the rolls when the process conditions are similar on both sides of the paper. Then the web does not know which roll surface to follow (***Fig. 6***). The web stealing can appear either on whole web width or just on the edges. It immediately causes streaks or pattern in the coated surface. The most sensitive situation for web stealing occurs when coating at high speed with equally hard rolls and with same coat weight on symmetric base sheet.

7.6 Controlling the web release

There is possibility to control the web release with the base paper properties, process parameters or the coating color formulation. The paper web generally follows the paper side with thicker color film or the film with higher cohesive resistance (i.e. dry solid content and viscosity).

The base paper properties like sheet openness and smoothness are most dominant regarding web release for the coat weight of 70 g/m^2. The more open base paper surface allows more coating to penetrate and thinner non-immobilized film then remains on the surface. The thinner non-immobilized layer reduces the resistance towards web release.

With a difference in roll hardness and certain speed difference between the rolls, it is possible to control the web release. The difference of 5-10 P & J in cover hardness induced this difference. The sheet tends to follow the harder roll due to less deformation and better surface contact. The softer roll deforms more in the roll nip resulting in less surface contact due to varied surface velocity. A slight speed difference between the rolls of about 0.5% can also be used to control the web release, where web follows the faster roll.

8.0 MODIFICATION OF THE SIZE PRESS DESIGN

There have been many modifications of size press design to avoid film splitting, nip rejection and other problems discussed above. Some are given below.

8.1 Gate roll size press

It has an offset pond, which is not in contact with the sheet. This offset pond feeds a metering nip which controls the amount of size going to a second nip. The second nip controls the film uniformity. The rolls in the gate roll train are run at different speeds to minimize film split patterning.
Substitution of a gate roll size presses for a conventional size press in values replacing two rolls with size contributing to increased initial investment and maintenance bit.

8.2 Blade/ rod metering size press

Short dwell blade coater heads are used to apply and met the size to the size press roll. This permits operation without a pond or with a very limited one.

8.3 Calender sizing

This is an important method of applying surface size to heavy weight papers and paperboards. It is possible to size these papers without dying because of the latent heat contained in the board when it reaches the calender stack. This heat causes some evaporation between the calender stack and the reel. The remaining water is absorbed by the board without a significant increase in the overall moisture content.

The pick up and distribution on the sheet is dependent on the surface roughness and moisture content of the paper, temperature and concentration of sizing solution, location of the boxes in the calender stack, penetration of the size into the sheet is favored and pick up rate will increase. Placement lower on the stack tends to reduce pick up and hold the size near the surface. The boxes may be placed on only one or both sides of the stack to treat one or both sides of the sheet. Some mills have two calender stacks a "wet stack" equipped with calender boxes and a "dry stack " to do final calendaring. There may be few dryers between the stack (***Fig.*** *7*).

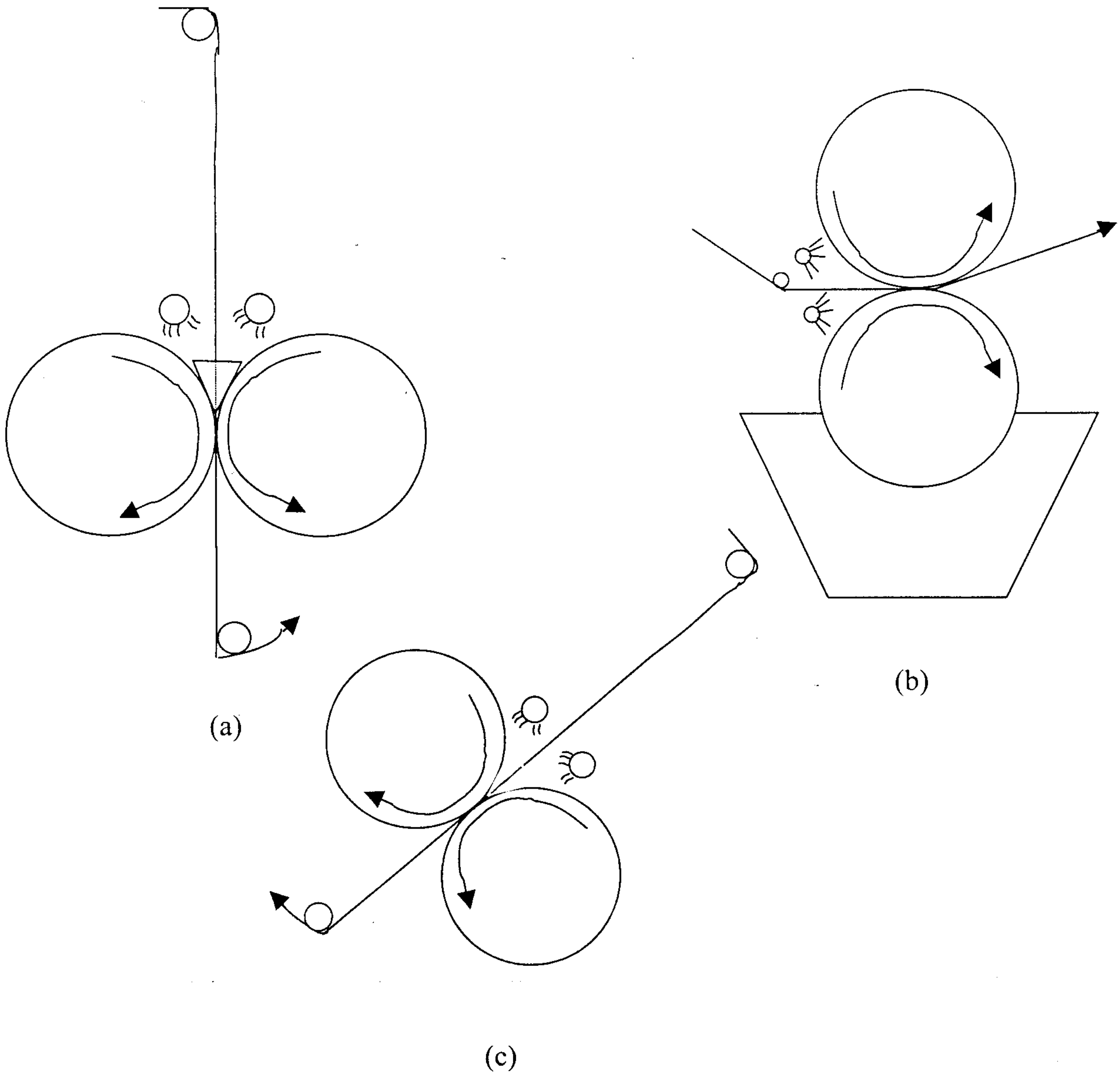

FIG. 1: POND SIZE PRESS CONFIGURATIONS WITH (A) HORIZONTAL, (B) INCLINED, (C) VERTICAL ROLL.

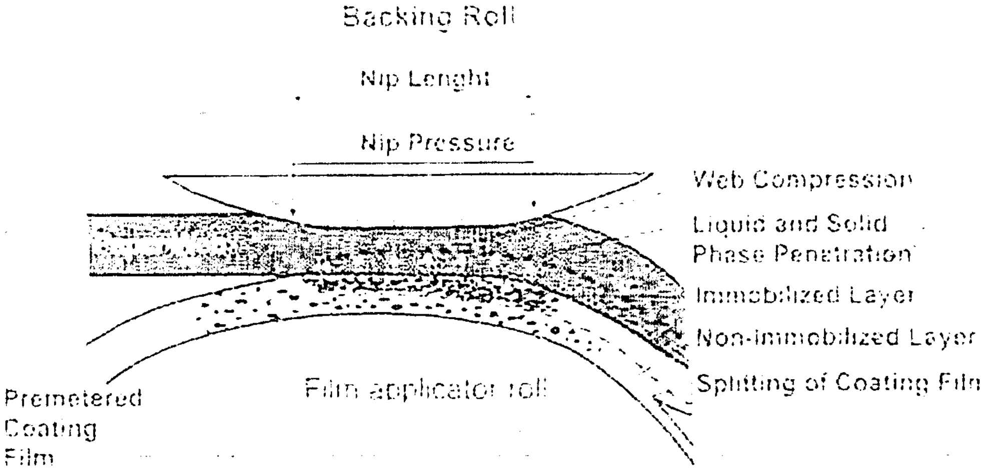

FIG. 2: TRANSFER OF COATING TO THE PAPER IN THE NIP BETWEEN THEFILM APPLICATOR ROLL AND THE BACKING ROLL.

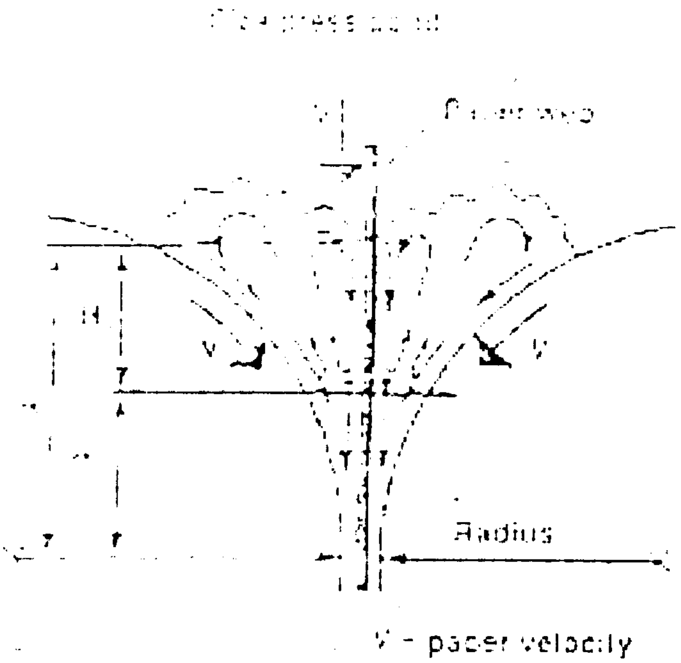

FIG. 3: HYDRODYNAMIC FORCE IN THE NIP

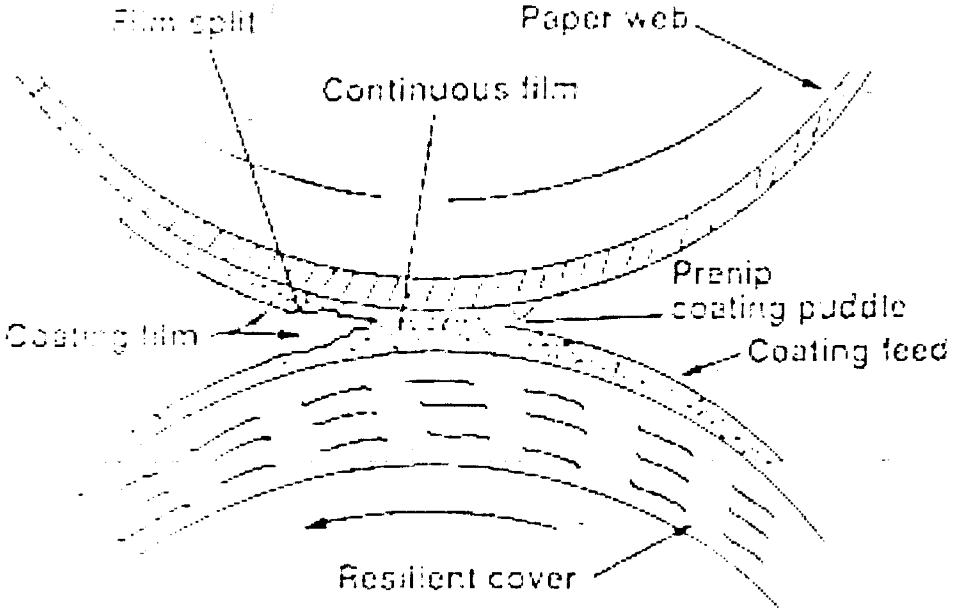

FIG. 4: DEVELOPMENT OF FILM SPLIT PATTERN

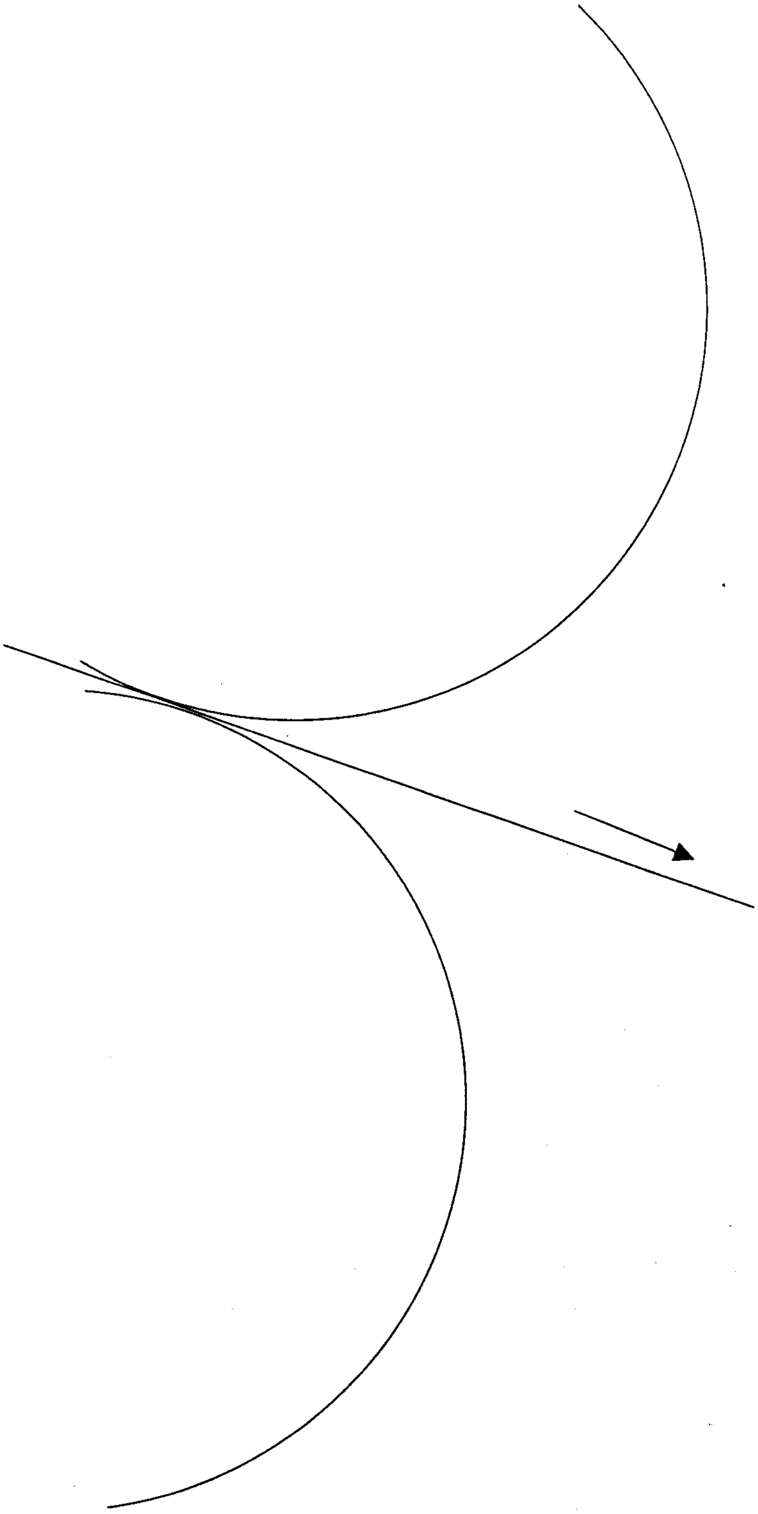

FIG. 5: COATING COLOUR MIST DUE TO FILM SPLITTING AT WEB RELEASE.

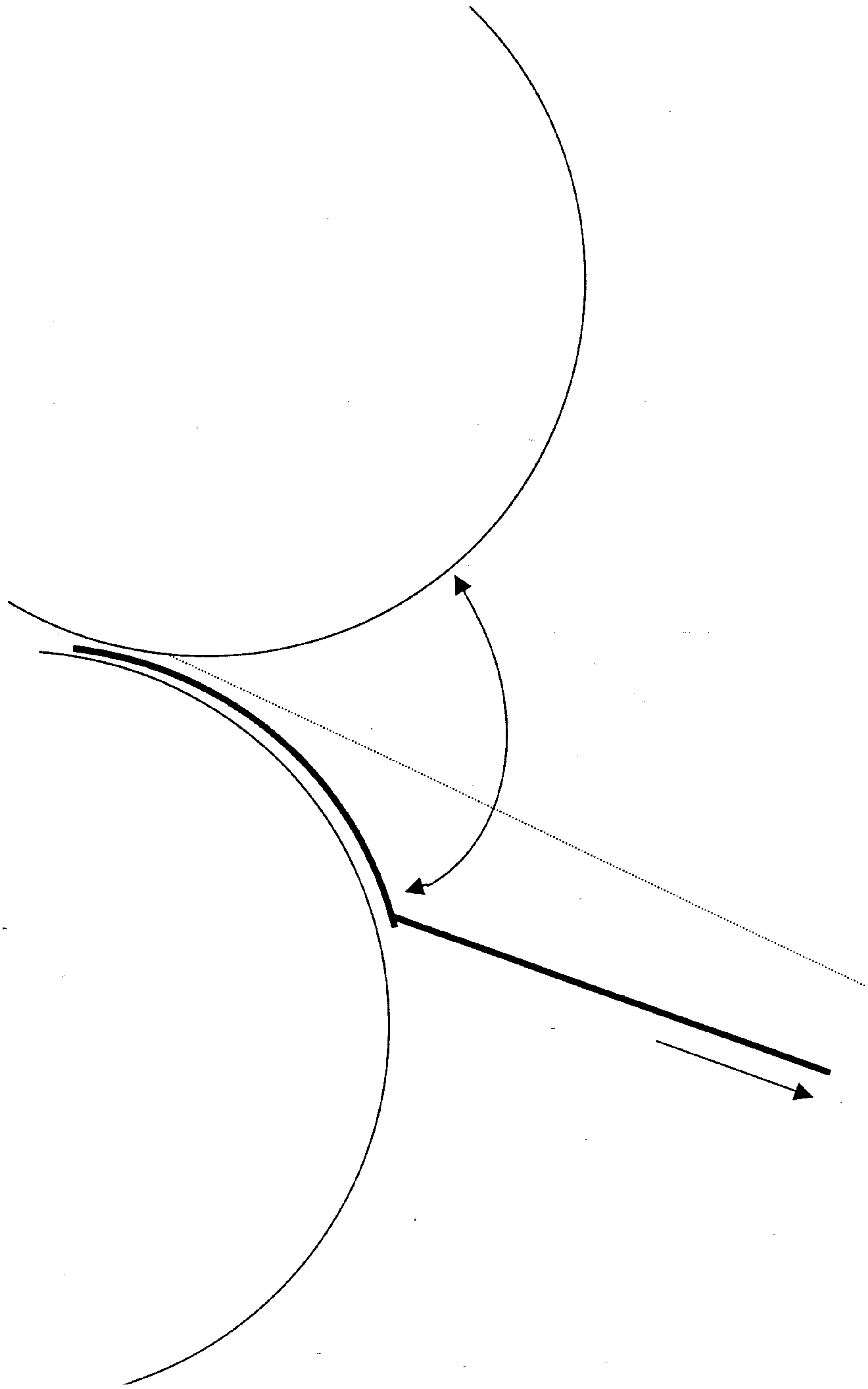

FIG. 6: WEB STEALING BETWEEN TWO ROLLS

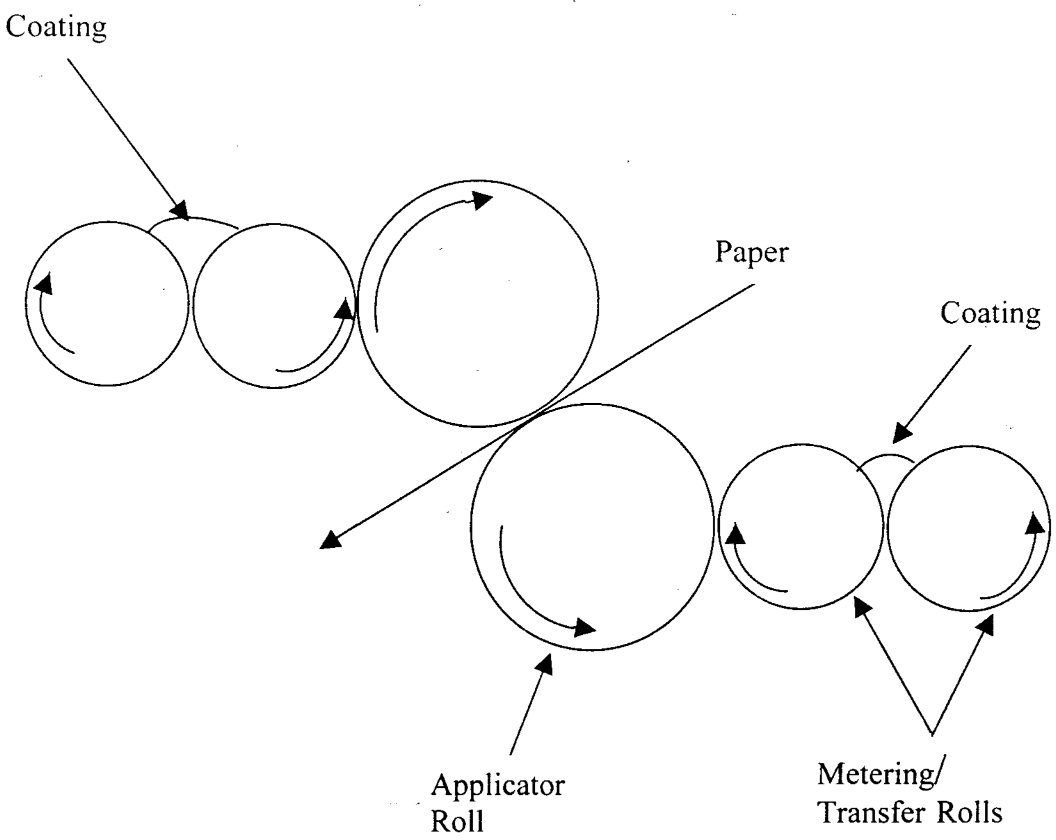

FIG. 7: GATE ROLL SIZE PRESS.

REQUIREMENTS OF BASE PAPER FOR PIGMENT COATING

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REQUIREMENTS OF BASE PAPER FOR PIGMENT COATING

Dr. Y. V. Sood

1.0 INTRODUCTION

Base paper quality is vitally important for any coating operation and is often given insufficient attention by the coated paper manufacturers. To ensure satisfactory results in coating it is essential that properties of importance for base paper are given proper attention. In this article the important properties which should be considered for base paper have been defined.

2.0 BASE PAPER REQUIREMENT

Some of the important properties for base paper are:

- Good level.
- Appropriate optical properties.
- Uniformity in grammage and thickness.
- Minimum number of joins/splices in reels.
- Free from holes, lumps or other contraries.
- Proper porosity.
- Properly sized.
- Proper moisture content.
- Low expansion when sheet is wet.
- Surface roughness and compressibility.
- Sufficient tensile and tear.

2.1 Good level

A coated paper manufacturer requires paper reels of good level i.e. straight-edged reels, without hard or soft edges, free from ribs, chains, pipes, twists, cockles, buckles and baggy areas. The paper passing through the coating head on the coating machine should be flat and evenly tight to get uniform coating. If it is not flat, then uneven coating will be applied which will give reels with non-uniform thickness at the coater rewind. Such papers while printing will pose lot of problems such as non uniform prints, non uniform expansion in offset printing presses leading to misregister of colours in the print.

2.2 Appropriate optical properties

The base paper should have reasonable level of brightness. The manner in which brightness is altered by coating with a coating formulation depends to a great extent on the brightness level of base paper. Change in brightness with increase in coat weight is usually higher, the larger the difference between the brightness of the base sheet and brightness of coating layer itself (***Fig.1***)

Coated papers will generally have somewhat higher brightness than uncoated base sheet, but in single coated paper the difference should not exceed 2 points as otherwise a brightness mottle will occur in blade coated papers. For a high brightness base sheet, a coating formulation containing ordinary coating clay gives a decrease in brightness on coating, whereas a base paper of lower brightness an increase is observed. Thus increasing the coat weight, in some cases could be an effective means of increasing the brightness, whereas, in other cases, it can be very expensive or even impossible to increase the brightness by increasing the coat weight. Such effect was observed while testing coated paper samples of a particular mill (table 1). It was observed that brightness of coated paper was 3.2 points lower than the base paper, which was having brightness of 78.6%. On the other hand the board sample manufactured by the same mill had higher brightness by 2.9 points as compared to its base board. The probable cause of brightness drop in coated paper was inefficacy of pigment to affect brightness level, whereas it had shown its effectiveness for board due to low brightness of base paper. Type of coating pigment, its particle size distribution and binder element also affect the brightness of coated paper. Air knife coating give a better and more uniform coverage resulting in a more uniform brightness of the coated paper or board. For example for beer packages, this effect is very much used in air knife coating of unbleached kraft board with high brightness TiO_2 colours.

In case of coated papers, the light scattering and light absorption of base paper and coating must be adapted so that the product has the desired properties. Opacity of coated paper has almost linear relationship with coat weight (***Fig.2***).

With the increase in coat weight the opacity level is increased. Generally ordinary clay gives an improvement of 2 to 3 points in opacity per 10 g/m^2 of coat weight. For the same coat weight, a coating of higher light scattering and/or higher light absorption gives a higher opacity. The light absorption must not be so high that the coating layer's own brightness becomes lower than that of the base paper, then the brightness will decrease. In order to achieve a high brightness of a dark base paper, the base paper must be optically covered i.e. the coating must have higher light scattering and high light absorption. If the base paper has high brightness, a coating with low light absorption will be able further to increase the brightness as explained below.

The coated paper can be considered as three-layered structure as shown in ***Fig. 3***. To calculate the reflectivity of coated paper using Kubelka-Munk equation it will be necessary to know the light scattering (S), light absorption co-efficient (k) and coat weight (x) of coating layer. Also the light scattering, light absorption and grammage of base paper is required. To get good optical covering ability, the light scattering of coating must be high. If the base paper already has a high reflectivity, a low light absorption in coating will further increase the reflectivity of paper (***Fig. 3A, Fig. 3B***). Higher binder content has negative effects on all optical properties in most pigment coatings (***Fig. 4***). This is due to the reason that the pores are filled with the same refractive index as the pigment and all the reflection and refraction, which build up the light scattering, are then absent. Pigment used for coating should have low binder demand to get good optical properties. The lowest amount of binder needed will be the best for the optical properties of paper. Some pigments such as Satin white in spite of having higher binder demand than others still gives coated papers of high brightness. The optical properties of coating are dependent on pigment and amount of binder. The pigments used in coating are of much smaller size. The refractive index of common pigments in coating are given in Table-II.

2.3 Formation and thickness

For base paper, uniformity in grammage i.e. formation and thickness are desirable. It is difficult to define the actual limits but a profile difference of more than 5 percent variation will pose problems like non-uniform coating, curling etc. The modern printing machines require that the thickness of paper sheets should not only be uniform in machine direction but it should be uniform in the cross direction also, otherwise serious troubles are observed in their runnability at the higher speeds. Paper that has a wild, non-uniform formation; tends to absorb coating unevenly, resulting in a mottled appearance. A variation of 2 percent opacity is enough to cause trouble if variation occurs within 2-cm interval.

2.4 Joins/splices in reels

Reels should have minimum number of splices. Frequent splices pose problems as they disrupt the coating film and in many cases resulting some length of poorly coated paper. Sometimes paper breaks at joins which lead to wash-ups as well as refeeding downtimes or they give wrinkles or pipes in the coated reels.

2.5 Free from holes, lumps and other contraries

Holes, lumps are highly undesirable in paper. Holes are detrimental for all types of coaters as the colour strikes through to the backing roll where it can cause a web break. Holes can cause breaks or allow coating to pass through them on to the backing and lead rolls. It also allow coating build up under the blade which will require more frequent cleaning. Dust and debris if present on paper will get into coating mix or under the metering device and cause streaks and possible breaks whereas lumps will disrupt the coating film again causing streaks.

2.6 Proper porosity

Porosity is especially important when two different types of coatings are to be applied on the opposite sides of sheet. If the porosity is high then both coatings are forced through and mix with each other. For example, the chemical in carbon less paper coatings on both sides if get intermixed will cause spoiling by colour development.

2.7 Properly sized

Sizing is an important characteristics for some base papers. If the base paper is soft sized it will absorb more coating. The paper should be sufficient sized so that major part of coating stays on the surface of sheet. On the other hand a hard sized paper will resist coating and proper binding of coating on the paper surface will not take place. Groundwood are TMP containing papers are generally not sized. In such paper, presence of lignin acts as sizing.

2.8 Proper moisture content

Moisture content of the base paper also influences the absorption of coating into sheet. The lowest moisture is needed to get proper coating. Around 4% moisture is considered appropriate. The moisture profile should also be uniform across the web.

2.9 Low expansion when sheet is wet

The most important of base paper is the dimensional stability when it is wet. Wet expansion is defined as the percentage expansion that a sample undergoes when it is immersed in water for one minute. Paper with high wet expansion will lead to numerous problems such as curls, pipers and wrinkles. Base paper having wet expansion ratio 2:1 in CD and MD directions are better. The higher expansion ratio will pose problems during coating.

2.10 Surface roughness and compressibility

Surface roughness of the base paper affects the gloss of air knife-coated papers. The development of gloss after calendering is dependent on the surface smoothness of the coated paper. Proper furnish and high smoothness of the raw stock are necessary to achieve even distribution of the pigment coating on the base paper. The need for smooth paper is obvious, but it should not be achieved by excessive calendaring, because it can result in uneven absorption of coating and thus causing variation in the thickness of coating. Binder and pigment influence the gloss of coated paper also. For instance, CMC Latex gives a higher gloss level than protein latex. The pigment particles size distribution and the type influence the gloss. Calcium carbonate with its irregular particles gives lower gloss than kaolin with its plate like particles.

Compressibility of paper influences the printing smoothness of the coated paper. Printing smoothness of coated paper is dependent primarily on the compressibility of the base paper and to lesser extent of the coating layer.

2.11 Tensile and tear

For satisfactory runnability of paper in coating machine the web must be strong enough to run through the coater without breaking or tearing. This, of course, applies in the wet state after coating as well as in the dry.

3.0 DOUBLE COATED FINE PAPER

For production of high bright, coated paper using relatively dark base paper, the first coating should contain pigment of high light scattering and high absorption. The top coating should contain pigment of low absorption to get better brightness (***Fig. 5***). Dyes and FWA are used both in base paper and in coating layer. The dyestuff added to the base paper influence the nuance of coated paper, as these coating layers are not opaque. FWA in the base paper can be important for the appearance of the final product. It can give a whiteness addition, which is not possible to attain by concentrating all FWA to the top layers.

The primary task of the coating is to improve the printability of the paper. Low surface roughness and a suitable oil absorption are important properties for good printability. High paper gloss is sometimes also desired, since the 'lustre' of the print surface is a positive printability property.

The paper gloss is promoted by choosing a gloss-giving pigment in the coating. The coated papers must further be calendered to produce the gloss. Clay pigments, which are flaky, give high paper gloss. Other pigment forms can also give high gloss- it is often a question of choosing sufficiently fine-grained pigments to attain gloss.

In certain cases, matt-coated products are desired, i.e. papers with an even surface but low gloss. A high gloss on the printed surface is often desired even on matt papers.

A high gloss is a condition for attaining the highest colour saturation on the printed sample. The glossy surface gives a very low scattering of the incident light. The light penetrates into the material which gives colour.

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TABLE-I

TEST RESULTS OF THE PAPER SAMPLES RECEIVED FROM A COATING PLANT

Property	Value obtained for sample					
	Base board	Coated uncalendered	Coated calendered	Base paper	Chromo coated uncalendered	Chromo coated calendered
Grammage (g/m^2)	174	205	206	64.8	78.5	76.9
Amount of coating (g/m^2)	Nil	31	31	Nil	13.7	12.1
Bulk (cm^3/g)	1.25	1.22	0.96	1.31	1.22	0.91
Tensile index						
CD	24.0	22.0	23.0	30.5	35.0	29.0
MD	44.0	39.0	40.5	50.0	44.0	45.0
Burst Index (kPa.m^2/g)	1.45	1.30	1.45	1.80	1.50	1.50
Tear Index (mN.m^2/g)						
CD	6.75	6.25	5.45	5.00	4.75	3.75
MD	6.45	5.50	5.25	4.55	4.25	3.40
Brightness (%)	73.1	79.0	76.0	78.6	77.3	75.4
Opacity (%)	97.7	99.7	99.3	81.4	91.6	88.3
Cobb (g/m^2)						
Top	16.7	—	—	19.5	—	—
Wire	18.5	—	—	20.4	—	—
Avg.	17.7	—	—	20.0	—	—
Smoothness, Bendtsen (ml/minute)						
Top	130	170	40	220	340	50
Wire	140	200	50	240	400	75

TABLE-II

REFRACTIVE INDEX OF DIFFERENT PIGMENT AND BINDER

Pigment/Binder	Refractive Index
Aluminium Oxide hydrate	1.57
Calcium Carbonate	1.5-1.66
Clay	1.57
Calcined Clay	1.60
Polystyrene Pigment	1.59
Talc	1.57
TiO_2, Rutile	2.76
TiO_2, Anatase	2.52
Styrene Butadiene	1.57
Starch	1.53

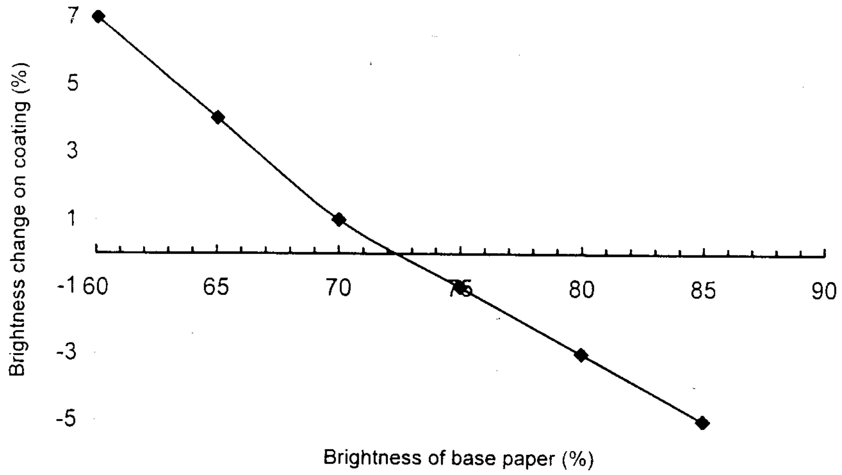

FIG. 1: EFFECT OF BASE PAPER BRIGHTNESS ON THE BRIGHTNESS OF COATED PAPER BY ORDINARY CLAY

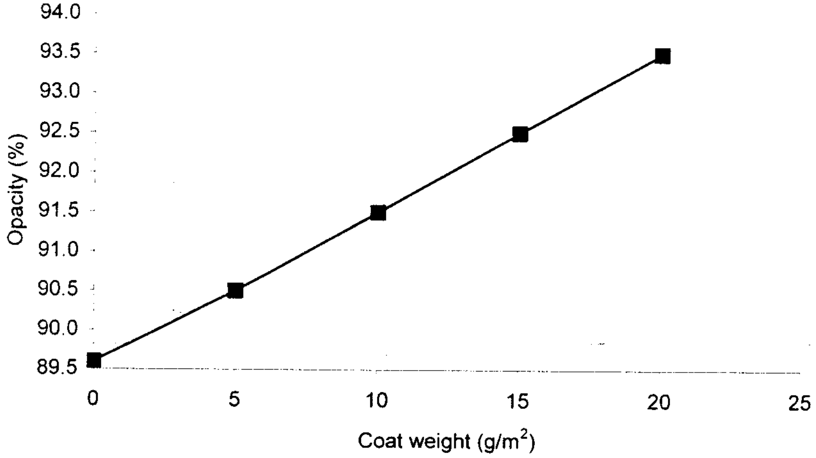

FIG. 2: EFFECT OF COAT WEIGHT ON THE OPACITY OF COATED PAPER

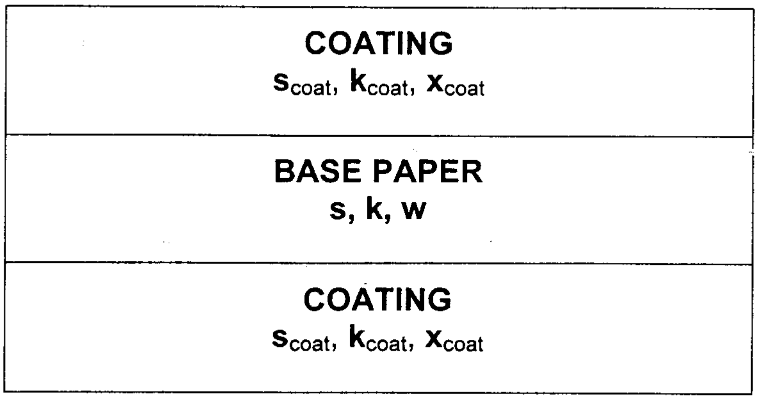

FIG. 3: MODEL OF COATED PAPER

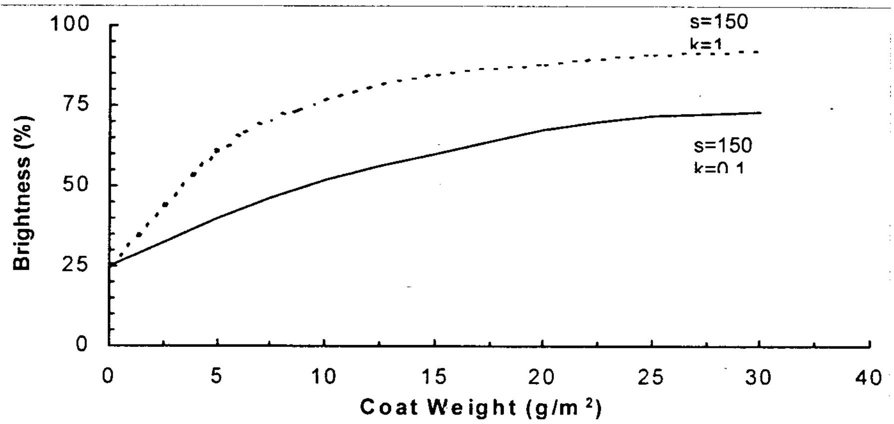

FIG. 3A: TO ATTAIN THE HIGHEST BRIGHTNESS ON DARK SUBSTRATE A HIGH LIGHT SCATTERING CO-EFFICIENT IS NEEDED

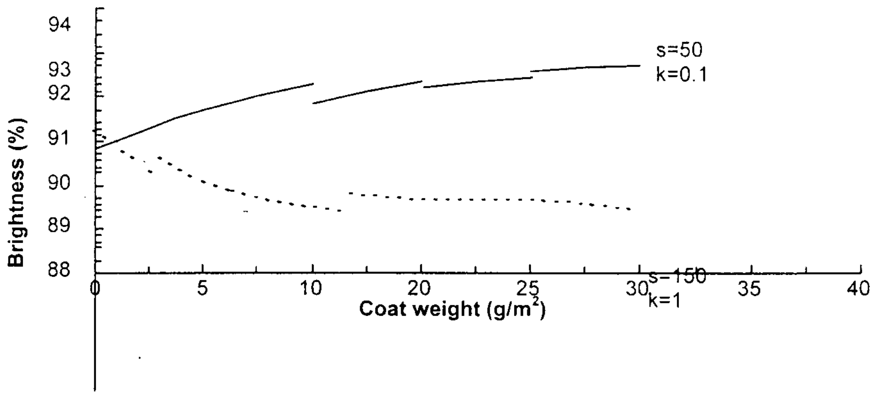

FIG. 3B: FOR A VERY LIGHT SUBSTRATE THE LIGHT ABSORPTION CO-EFFICIENT OF COATING IS ALSO IMPORTANT

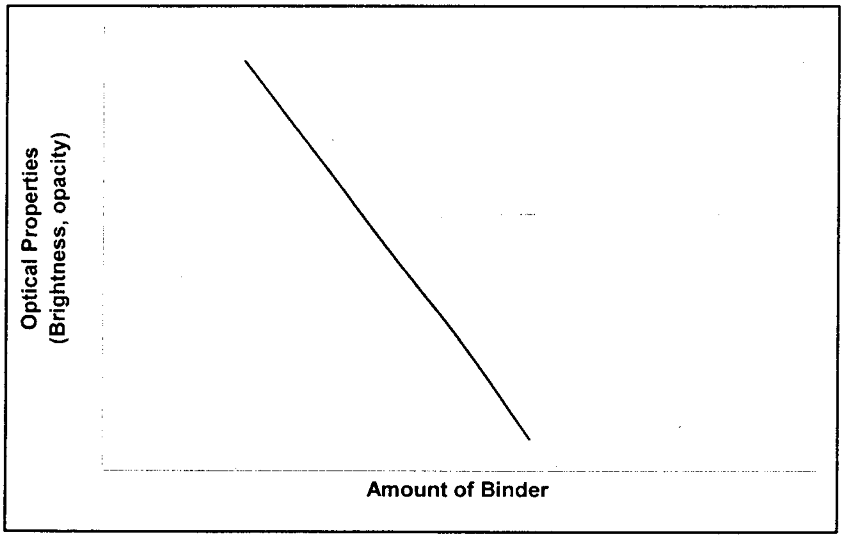

FIG. 4: EFFECT OF BINDER LEVEL ON THE OPTICAL PROPERTIES OF COATED PAPER

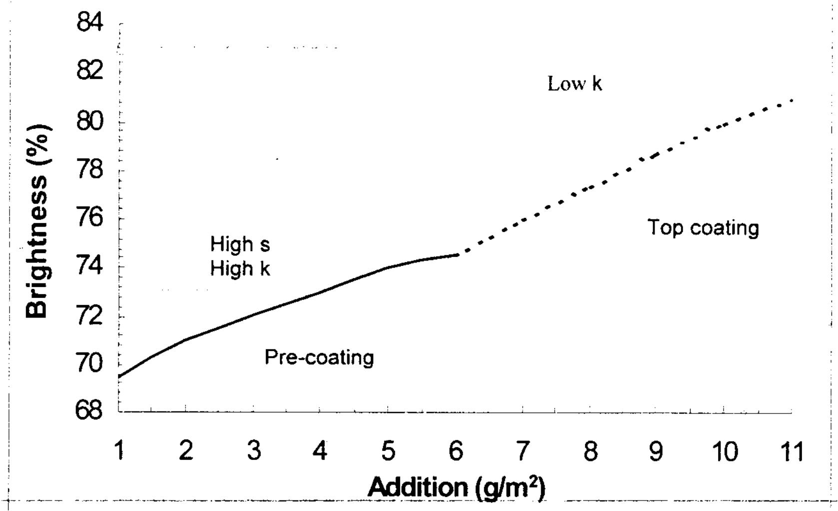

FIG. 5: DOUBLE COATED FINE PAPER

COATING

COATING COLOUR INGREDIENTS AND COATING FORMULATIONS

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COATING COLOUR INGREDIENTS AND COATING FORMULATIONS

Y. V. Sood

1.0 COATING COLOUR INGREDIENTS

Coating colour ingredients generally are:

- Binders
- Pigments
- Foam controlling agents
- Water retention & rheological modifier
- Colours
- Dispersants
- Insolubilizer
- Biocides

The coating colour characteristics depends on the following final requirements:

1.1 End product requirements

Printing process (sheet offset, web offset, letter press, gravure)
Other requirements (varnish, bronze, emboss etc)
Physical (strength, stiffness)
Optical (Opacity, brightness, shade)

1.2 Raw stock constraints

Furnish selection
Internal sizing
Surface sizing
Formation

1.3 Equipment Constraints

Rheology
Water handling
Drying rate

1.4 Cost constraints

Raw materials
Coater speed limitations

2.0 BINDERS

The common binders used in pigment coating are:

2.1 Starches

Starches are of following type:

- Enzyme converted
- Thermal chemical converted
- Oxidized (chlorinated)
- Hydroxyethyl ether
- Others (acetate, cyroethyl, cationic, thin boiling)

The advantages and disadvantages of starch are:

2.1.1 Advantages

- Economics
- Availability & variety
- Good adhesive strength per unit cost
- Good rheology
- Ease of attaining desired viscosity
- Blends with many latexes and PVA
- Good heat and light stability (does not discolour)
- Low odours
- Good blister resistance (more than latex)
- Water receptivity (improve printing properties in web offset printing)

2.1.2 Disadvantages

- Binder migration (Mottle)
- Difficult to insolubilize (Low wet pick)
- Low gloss
- Film tends to be brittle (dusting & cracking at folds)
- Retrogradation – viscosity increase/decrease on storage.

Comparison of different modified starches in coating

Property	Enzyme converted	Thermal	Oxidized	Ethylated
Viscosity stability	Fair	Fair	Excellent	Good
Binding capacity	Fair	Good	Good	Excellent
Colour	Good	Fair	Good	Excellent
Economy	Excellent	Excellent	Good	Fair
Pigment dispersion	Poor	Poor	Excellent	Poor

2.2 Proteins

These are:

- Soybean extract
- Casein (from skim milk)
- Others (Animal glue, gelatin)

The advantages and disadvantages of protein are:

2.2.1 Advantages

- Excellent glueability
- High stiffness
- High opacity
- Excellent binding strength
- Excellent runnability on coating machine
- Improves stability and water retention of high latex level coating
- Good dispersing agents for pigments
- Adds blocking resistance

2.2.2 Disadvantages

- High viscosity of liquid coating at high solids
- Brittle films
- Foam stabilized in coating
- Odour
- Low gloss coating
- Low brightness coating
- Cost
- Must be cooked with alkali to prepare

2.3 Synthetic Latexes

These are suspensions of 100 to 200 nm particles in water. These commonly used latexes are:

- Styrene butadiene polymer
- Vinyl acetate polymer
- Acrylic polymer
- Alkali sensitive latexes (swollen by dilute alkalis)
- Latex starch solution

2.4 Synthetic soluble binders

These include:

a. Polyvinyl alcohol
b. Carboxymethyl cellulose

3.0 LATEXES

Following three latexes are commonly used
- Stryrene butadiene
- Polyvinyl alcohol
- Acrlyrics

Comparison of these latexes is as under:

3.1 Styrene butadiene Latexes (carbohydrate)

3.1.2 Advantages
- Excellent overall properties
- Gloss ink holdouts
- Bonding strength
- Wet rub and abrasion resistance
- Gloss

3.1.3 Disadvantages
- Glueability
- Blistering tendencies
- Odour
- Mottle

3.2 Polyvinyl Acetate Latexes (Co-polymers)

3.2.1 Advantages
- Brightness and brightness stability
- Stiffness
- Blistering resistance
- Hydrophilic

3.2.2 Disadvantages
- Ink holdout
- White pitch
- Low binding strength

3.3 Acrylic Latexes

3.3.1 Advantages
- Excellent overall properties
- Excellent runnability
- Brightness and brightness stabilities.

3.3.2 Disadvantages
- Very high cost

If we compare the binding performance per unit of cost then the rankings of different binders are as follows—

Binder	Rank
Starch	1
S. B Latex	2
Protein	3
Acrylic Latex	3
PVAC Latex	4
PV Alcohol	5

Binder requirement depends on the type of raw stocks, method of coating and printing. Generally the dosages of binder used are—

Printing method	Sheet requirement	Binder (Solid per 100 part pigment)
Sheet offset (Tackiest oxidizing type printing ink)	High gloss Good water resistance High gloss ink holdout High picking	14-20 (Latex exceed 50% with co-binder starch, casein)
Web offset (Heatset ink)	Dry & Wet pick resistance lesser than sheet offset	12-80 (Latex is 25-35%)
Sheet letterpress (Less tacky ink)	Wet pick resistance not required	8-16
Web letterpress		10-16
Rotogravure (Fluid ink)	No pick resistance	7-12 (Starch as main binder alongwith small latexes)

4.0 PRINTABILITY VS. LATEX PROPERTIES

Printability can be defined by the combination of press runnability and print quality. Although press runnability and print quality are closely interdependent, the former is more concerned with how fast and how long a printing press can be run trouble-free, while the latter is more concerned with the quality of image reproduction, print gloss, print mottle, back-trap mottle, water repellency, missing dots etc. Some of the important latex properties affecting print quality are discussed below.

5.0 INK GLOSS

Ink gloss depends not only on the unprinted initial sheet gloss, but also on the surface porosity and ink-binder interactions. Generally, the higher the initial sheet gloss is, the higher is the ink gloss. Ink gloss increases with decreasing latex particle size, suggesting that the ink gloss improves with decreasing interactions between latex polymer and ink solvent. This finding is also supported by the effect of acrylonitrile content of latexes on ink gloss; the higher the acrylonitrile is, the less is the interaction between the latex polymer and ink solvent and the higher ink gloss.

6.0 INK RECEPTIVITY AND INK ABSORPTION

Ink receptivity and ink absorption are two important properties of coated papers to be printed. There are a number of factors affecting the ink receptivity and ink absorption of coated surfaces, but the most important factor is the binder level in the coatings: the lower the binder level is, the higher the receptivity and absorption of ink are. Among different types of latexes, PVAc latexes are more ink receptive than either SB latexes or acrylic binders. Generally, ink receptivity increases with increasing latex particle size and increasing hardness of latex polymers. Also, it can be increased by limiting the coalescence of latex particles.

7.0 WEB OFFSET BLISTER RESISTANCE

Web offset printing requires a blister resistance of coated papers during drying the printed papers. PVAc latexes are more blister resistant than either SB or SA latexes. Although PVAc produce more porous coatings, the porosity is not the only reason for their excellent blister resistance. Their high thermal flow behaviors are responsible for blister resistance. Based on this finding, blister resistant SB latexes were developed by reducing their cross linking density. Many studies have been made on the effect of the gel content of SB latex polymers on blister resistance. The blister resistance of SB latexes improves with their decreasing gel content. However their bonding strength also decreases with decreasing gel. Therefore, blister resistance and binding strength are often compromised for the development of blister resistant SB latexes. The effect of gel content on both the blister resistance and binding strength of SB latexes.

8.0 ROTOGRAVURE PRINTABILITY

Rotogravure printability depends mainly on the transfer of ink from recessed cells to paper at the printing nip. Therefore, rotogravure printability requires both good fiber coverage and high compressibility of coated papers. As mentioned earlier, good fiber coverage and coating smoothness can be achieved by controlling the interaction of latexes with pigments or the colloidal stability of coating formulations, thus lowering their immobilization points. Although good fiber coverage is essential, it alone might not be sufficient for good rotogravure printability. The effect of latex polymer softness on missing dots is: the softer the latex polymer is, the better the rotogravure printability is in terms of missing dots.

9.0 FOAM CONTROLLING AGENTS

Three major types of antifoam/defoamers are available for coating – Water based, Oil based and polymeric. Water based ones are particularly susceptible to voids 'fisheyes'. Cylinder board mills using furnish contaminated with wax or oil and air-knife coating application found this type of antifoam of particular value because water based products did not further aggregate the 'fisheye' conditions.

Oil based compositions are most generally used compositions for coating applications because they seem to be most adaptable and versatile, both for chemical formulations and the user using paraffin oil as a base. The formulator adds hydrophobes as required depending upon the end use. The polymeric type products are the choice when formulator does not want to use an oil based composition and finds water based composition less effective.

10.0 WATER RETENTION AND RHEOLOGY MODIFIERS

Water Retention and Rheology Modifiers (WRRMs) are used widely in paper coating. The primary function is to provide the water retention and rheology control. These functions are known to play an important role in determining the runnability, coat weight and optical/mechanical properties of furnished coated paper or paperboard.

Commonly used WRRMs are:

- Alginates
- Cellulosics (CMCs, HECs)
- Polyacrylates

10.1 Alginates

Algin is a natural polysaccharide when it's formed on brown seaweeds of the group 'Phaeophycca'. These are processed to form various grades of alginates. It promotes water retention in coating. It exhibits low penetration into process substrates. The high water retention properties of alginate are well suited for bleached board coating, which are applied at relatively low speed and high solids.

10.2 Carboxy Methyl Cellulose (CMC)

CMC forms stable solutions over a broad range of pH. It is more tolerant of calcium ions than sodium alginate and does not require chelating agents for use in paper coatings. Usually low to medium type CMC's viscosity give higher water retention than high viscosity CMC. CMC is the predominant WRRM employed industrially free sheet paper coating formulation. It is also employed in some bleached board coatings. CMC has found little utilization in LWC papers due to use of starch as the primary binder.

10.3 Hydroxy Ethyl Cellulose (HEC)

HEC is a non-ionic water soluble derivative of cellulose. There are some essential differences between HEC and CMC. HEC has been found to absorb the Kaolin clays to a greater extent than the corresponding CMC. HEC has been reported to give higher K & N rank absorption as compared to CMC. These are desirable in some board grades and rotogravure coating formulation. HEC is employed industrially in free sheet, bleached board and recycled board coating applications.

10.4 Polyacrylates

Polyacrylate emulsions are petroleum based products and are used in coated paper and paperboard. The dosage is 0.15 to 1.0 parts per hundred parts pigment. The emulsion is usually added last to the coating colour to thicken the coating to the target viscosity.

11.0 COLOURS

Various types of colourants are used in water based paper coatings to produce a wide range of coloured papers ranging from tinted white to deeply coloured specialty grades. The choice of colourants depends on—

- End use requirement such as brightness, various light and chemical fastness.
- Compatibility of the colourants with coating slurry
- Ease of handling.

It must be remembered that Fluorescent Whitening Agent (FWA) effectivity is adversely affected by TiO_2 as it is a strong absorber of UV light. Of the two types available, anatase and rutile, the Anatase is preferred for use with FWA, as rutile absorbs more visible light A more economical approach in place of TiO_2 to increase opacity will be used higher percentages of clay and aluminium trihydrate. White clay does absorb some energy but it is lower than TiO_2.

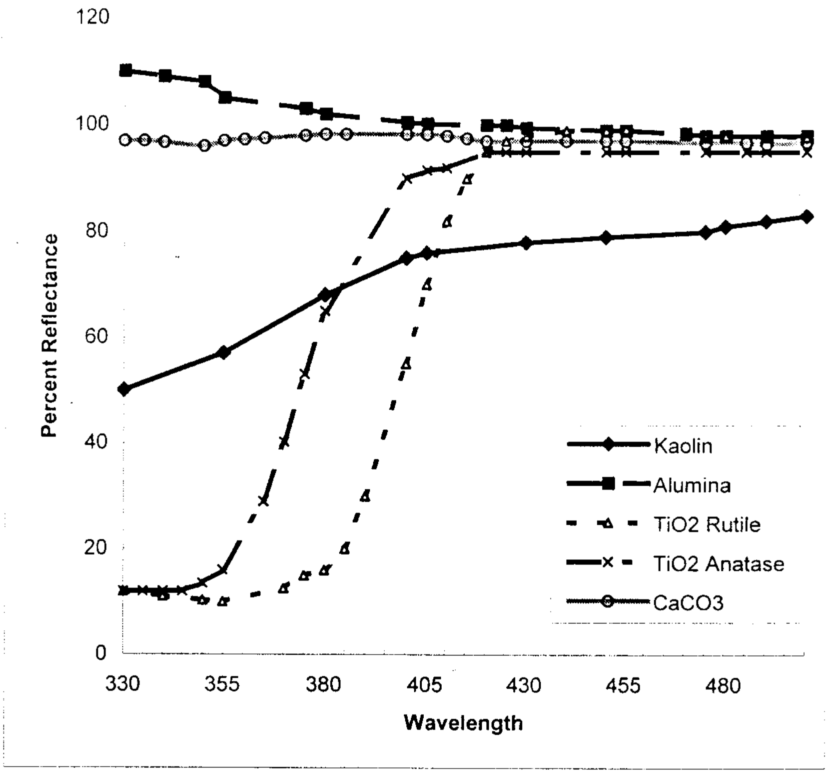

FIG. 1: REFLECTANCE CURVES OF TITANIUM DIOXIDES VS. OTHER MINERALS. CURVES ILLUSTRATE ABSORBANCE IN U. V. REGION BELOW 380 nm.

13.0 DISPERSANTS

Dispersants are chemicals used in deflocculation process of coating pigments. The dispersants usually are

- The anionic polymer dispersants
- The polyphosphate
- The alkali silicates
- The alkalis
- The non-ionic polymer dispersants

To evaluate any dispersant a pigment dispersant demand curve should be plotted.

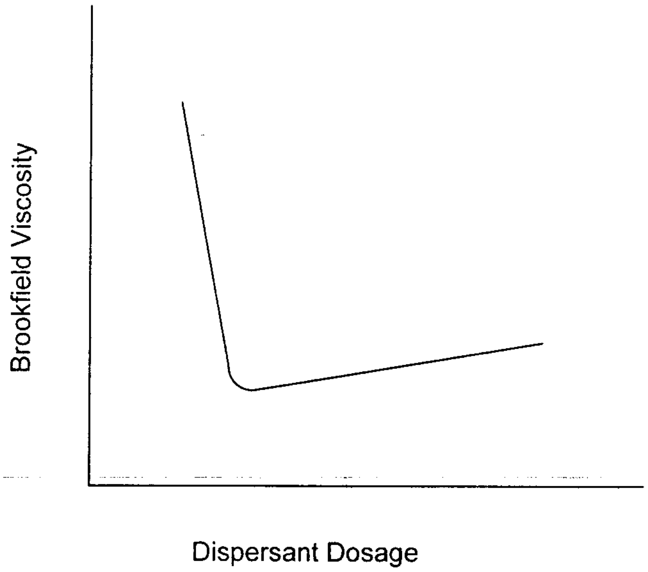

FIG. 2: PLOT OF BROOKFIELD VISCOSITY VERSUS DISPERSANT DOSAGE

It can be seen that with the increase in dispersant dosage firstly viscosity decreases rapidly at first, then a viscosity minimum occurs at the optimum dosage. The viscosity gradually increases beyond dosage. The viscosity minimum signals the optimum dosage of dispersant for specific system and conditions.

14.0 INSOLUBILIZERS

Paper coating insolubilizers are primarily used to reduce water solubility of pigment binders used in the coating. Water resistance is important for many applications of coated paper or paperboard on which the coated substrate may sometimes be moistened. Wet rub and wet pitch resistance are important for offset printing process.

The insolubilizers used by coaters and their dosages are—

- Formaldehyde (0.5-5.0%)
- Glyoxal (0.25-5.0%)
- Hexamethylene Tetramine(2.0-8.0%)
- Dimethylol Urea (2.0-10.0%)
- Urea Formaldehyde (2.0-5.0%)
- Melamine formaldehyde (1.0-4.0%)

15.0 BIOCIDES

Deterioration or spoilage of paper coating mixtures and ingredients used show up as loss viscosity, change in pH, odour development or change of colour. Different chemical preservatives used are organosulfur compounds, organohalogens, phenolic compounds, heterocyclic nitrogen compounds etc.

16.0 TYPICAL COATING FORMULATIONS ARE—

16.1 Formula No. 1

Components	Composition
China Clay	750 parts
$CaCO_3$	150 parts
TiO_2	50 parts
Soapstone	50 parts
Polyphosphate	3 parts
Starch	90 parts
Latex (SBR 50% solid)	30 parts

The coating mixture will be of about 58% solids.

16.2 Formula No. 2

Components	Composition
China Clay	940 parts
TiO_2	60 parts
Polyphosphate	03 parts
Latex	100 parts
Starch	100 parts
Casein	0.5 parts with ammonia

The coating mixture will be of about 58% solids.

17.0 REFERENCES

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COMMONLY USED COATING TECHNIQUES: THEIR ADVANTAGES AND DISADVANTAGES

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COMMONLY USED COATING TECHNIQUES: THEIR ADVANTAGES AND DISADVANTAGES

Y. V. Sood

1.0 COMMONLY USED COATING TECHNIQUES

Commonly used coating techniques in Indian paper mills are

- Air knife coating
- Blade coating

1.1 Air Knife Coating

The general layout of an air knife coater is shown in ***Fig. 1*** . The main elements are

- the applicator
- the air jet doctoring device
- the recovery system for metered off coating

The application system is usually a roll that turns in a pan of coating and which delivers an excess coating to the web . The air doctor is a slotted nozzle that projects a jet of air against the web to remove the excess coating .The shear rate of air knife metering is dependent on line speed (S) and thickness of wet coating film (t) and the relationship is

$$\text{Shear Rate} = \frac{S}{t}$$

It is essential that the air supply be free of particulate matter and be cool to 24 to 26°c .The low temperature is needed to minimize dehydration of the excess coating mixture supply system . The air knife meters the coating layer and reduce non uniformities at the application nip.

The effect of different operational parameters on the coat weight are:

Variable	Coat weight
Increase in air pressure	Decrease
Increase in gap	Increase
Increase in jet angle	Decrease
Applicator roll speed increase	Increase
Coating viscosity or solid content increase	Increase

Typical Air knife coater operating parameter for paper board are :

Air pressure (kPa)	About 60
Lip opening (mm)	Less than 1.0
Gap (mm)	2-5
Jet angle (degree)	35-45
Coating solids (%)	40-48
Speed (fpm)	800-1000

Coat weight in air knife coater is normally controlled by changing the air pressure. Within narrow limits , the coat weight can be influenced by the width of nozzle aperture, but this becomes ineffective for opening larger than 1.5 mm . Other variables that control coat weight are coater speed , coating mixture viscosity and coating mixture solids . An increase in any of these variables will result in an increase in coat weight . The air knife can apply about 10 to 24.5 g/m^2 to paper per side .

The advantages and disadvantages of air knife coating are:

1.1.1 Advantages

1. Applicability to wide range of raw stocks and coating condition , uniformly coat rough stock also.
2. No scratches .
3. Low mottle on printing .
4. Easily adjustable for changes in web widths , viscosity and solid contents of coating mixture .

1.1.2 Disadvantages

1. It is low viscosity and low solids operation . Normal coating solids range from 30 to 50 % , average is 45% .
2. Higher drying cost due to low solids .
3. Cleaning , compressing and cooling of air increases the cost .
4. Plugging of air slit .
5. Foam generation .

1.2 Steps to control coating defects in Air knife coating

Defect	Cause	Remedy
Orange peel	Binder migration , non-uniform coating layer from applicator nip .	Adjust applicator zone to avoid film splitting , Control drying
Fish scale	Operating the applicator roll at wrong speed or depositing insufficient amount of coating	Adjust speed

Slug and streak (Bump of coating)	Slugs are due to worn lips at the nozzle or inappropriate gap . Streaks occur when air knife is close to web	Check angle
Skips	Poor contact of the web with the applicator roll .	Adjust tension .

2.0 BLADE COATING

Blade coating is used mainly for the pigment coating of printed paper , but it is finding increased use for the application of functional coatings such as hold out , barrier release and encapsulated coating . The blade coater consists of a rubber covered back up role , generally 90-125 cm in diameter , against which a flexible steel blade is mounted .

The coating applicator should fulfill the following requirements

- Carry complete coating coverage.
- Minimum coating penetrated into web .
- Application of pre-metered coating film so that least amount of blade pressure is needed.
- No excessive drag against the web .

The different applicators used are:

- Flooded nip
- The two roll
- Fountain applicator

2.1 Flood Nip

The schematic is shown in ***Fig. 2***.

2.1.1 Advantages

1. Good wetting of substrate
2. Low drag against web
3. Simplicity
4. Relative ease of cleaning

2.1.2 Disadvantages

1. Poor deckle control
2. Poor pre-metering
3. Film split pattern
4. Foam generation
5. Coating strike through

2.2. Two roll coated in flood nip

In two roll coating the two rolls pre-meter the amount of coating before it is applied to the web (Fig. 3) . The advantages are

- A pre metered amount of coating is delivered to the blade
- Skips of coating are less .
- No film-split pattern to the blade
- The applicator nip does not develop hydraulic pressure which give less coating strike through .

2.3 Fountain feed

Fountain feed system is shown in ***Fig .4*** . This consists of a hollow beam with a slot formed by a set of adjustable lips on the top side . The slot is set to 1-2 mm from the moving web . Good foam control is needed for proper operation of the fountain .

Advantage is that the less hydraulic pressure is generated in the coating against the web compound to a single roll application which results in less penetration of coating in to paper .

3.0 PUDDLE COATER

This coating method is combination of applicator and blade in a single unit (Fig. 5) . It consists of a box filled to a back up roll face where the lower roll to box seal is a trailing blade. It is simple in design and has very short soak in time , which minimize scratch problem . But coating turbulence can be problem at high speed .

Another development is from a rigid blade holder to an air cushioned or pneumatic blade holder (Fig.6) .

Advantages are:

- Heavier coating possible
- Forgiving to paper defects
- Less blade wear
- Coat weight and blade angle can be changed while running
- Can give better blade effect i.e. butter action

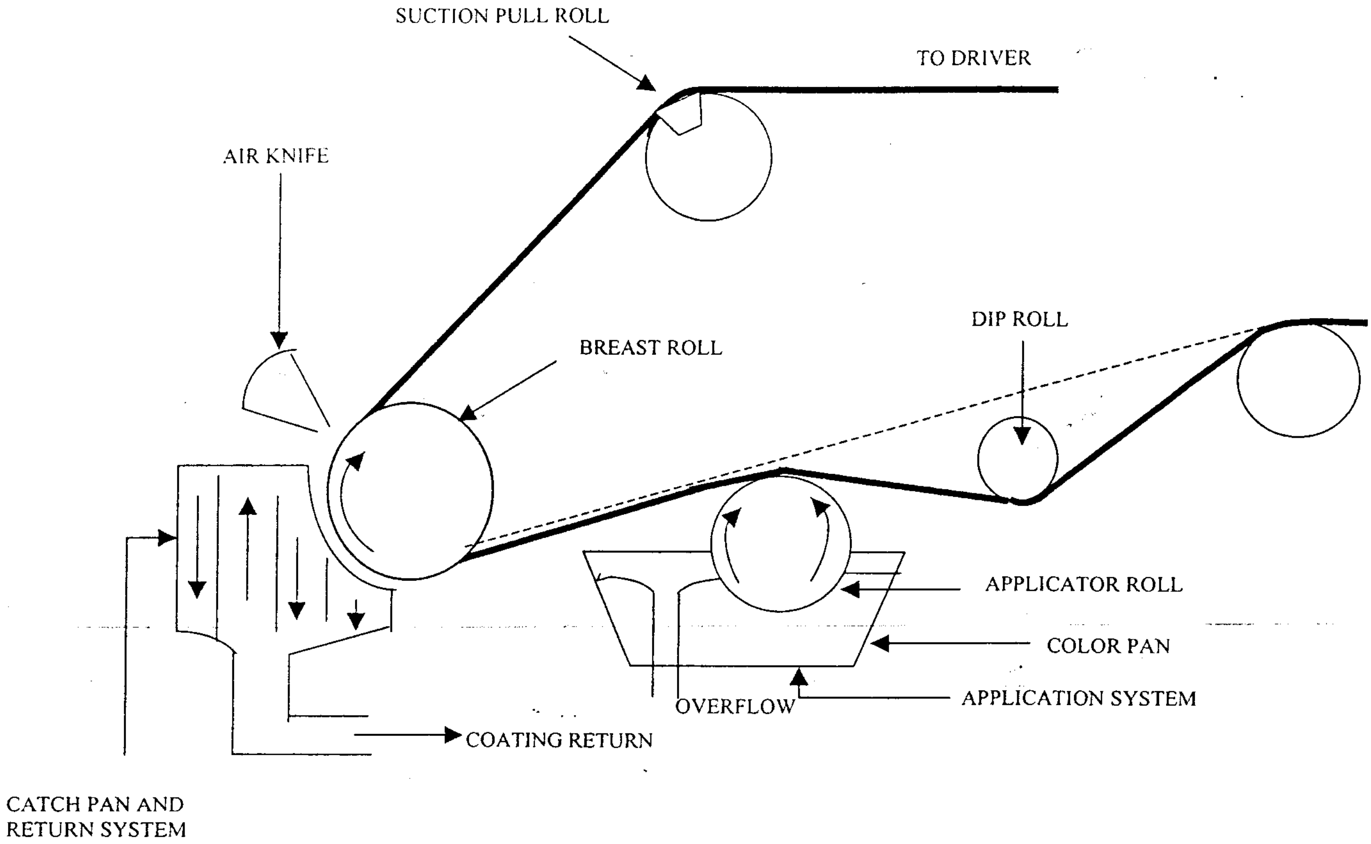

FIG. 1 GENERAL LAYOUT OF THE AIR KNIFE COATER

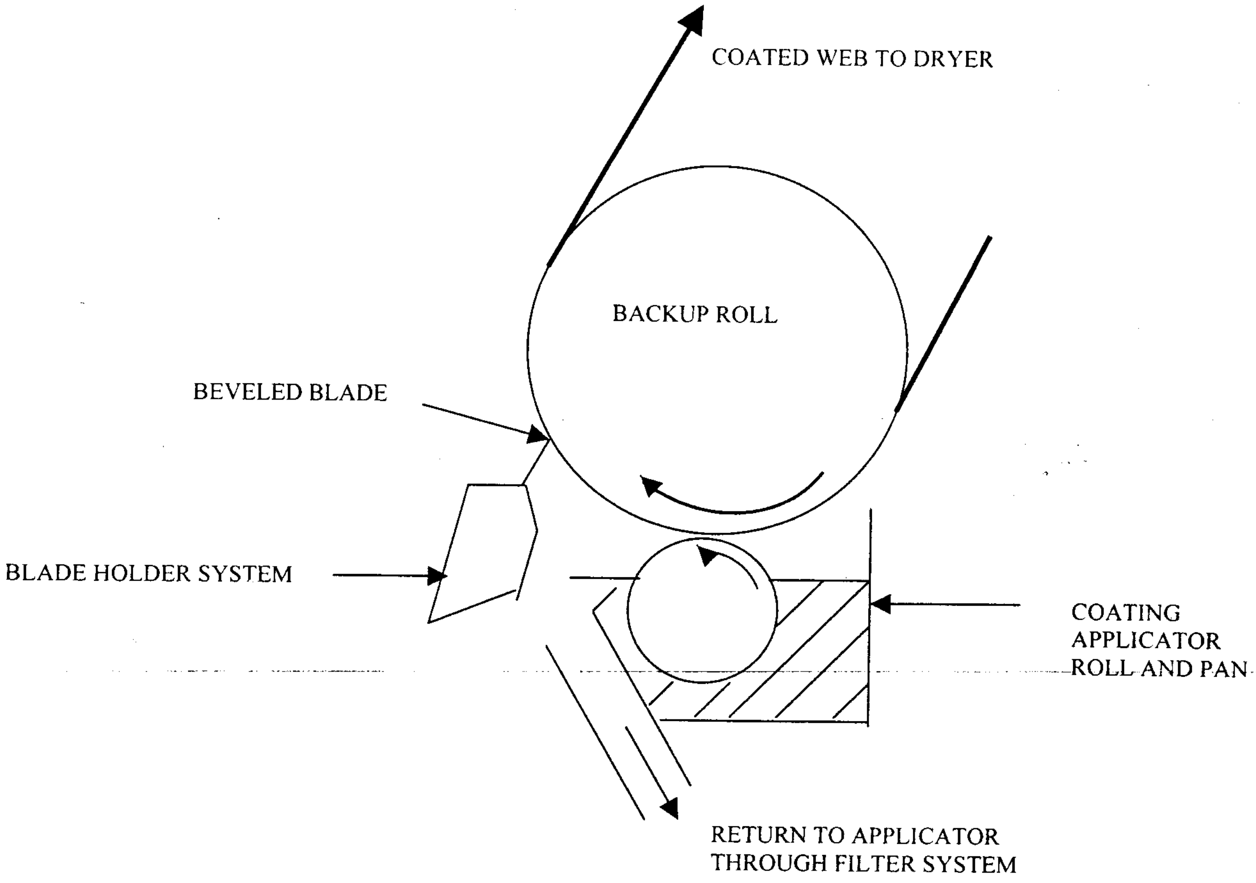

FIG. 2: INVERTED BLADE COATER USING FLOODED NIP.

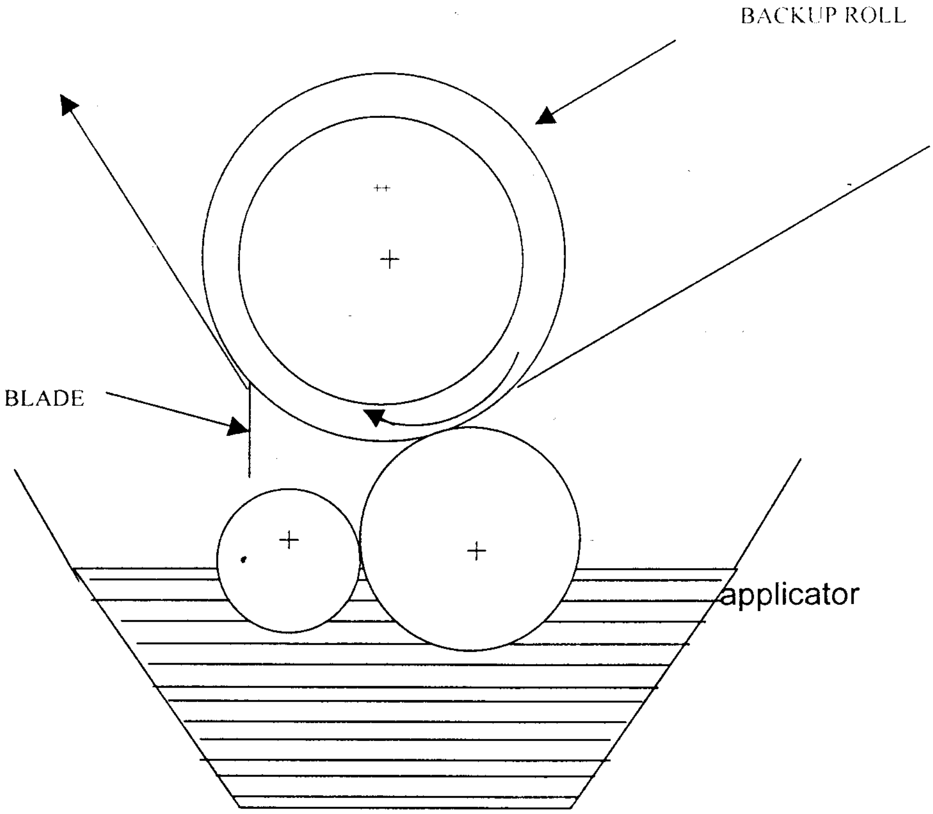

FIG 3: INVERTED-BLADE COATER USING TWO-ROLL APPLICATOR.

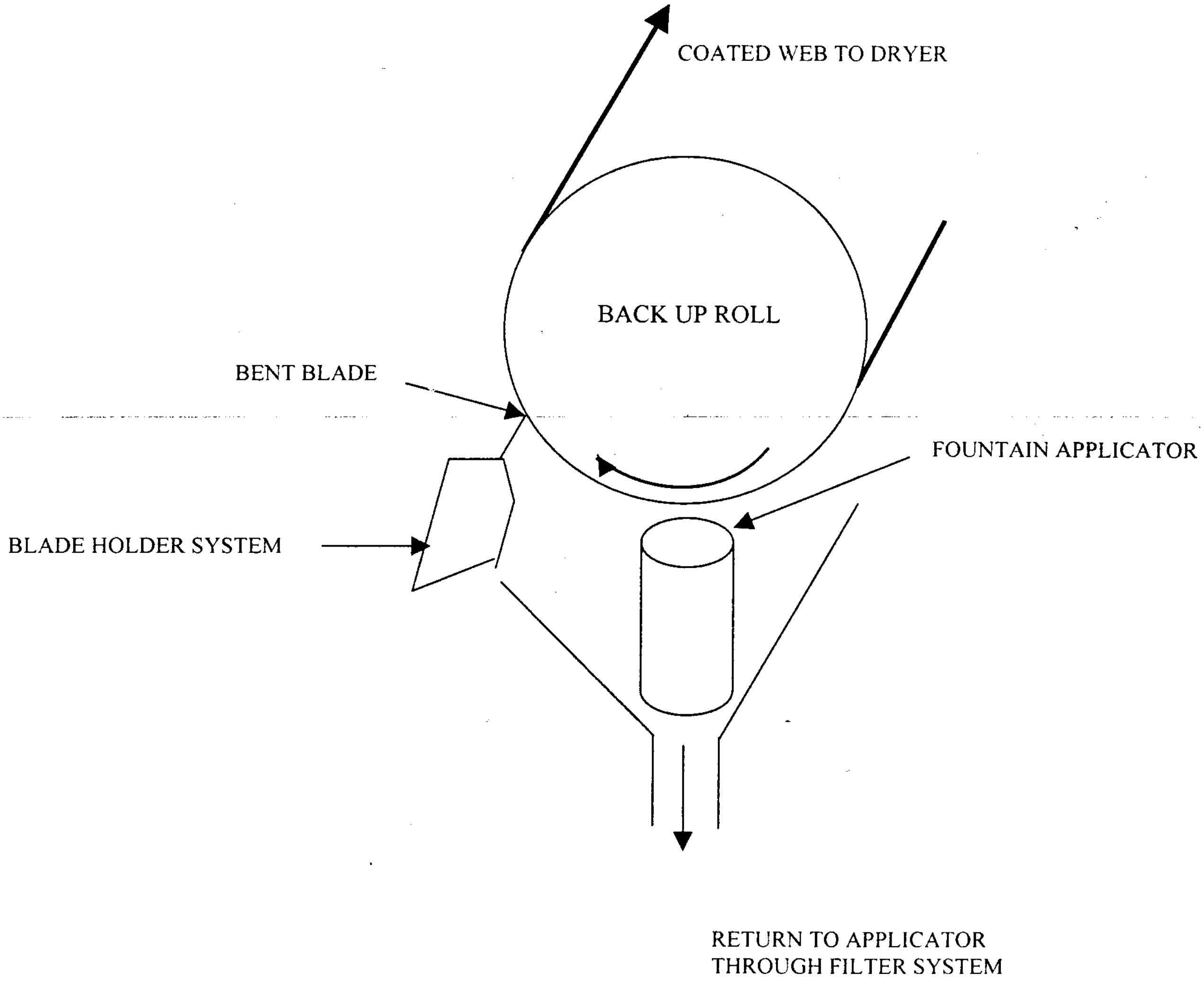

FIG.4: BLADE COATER BENT BLADE WITH FOUNTAIN APPLICATOR

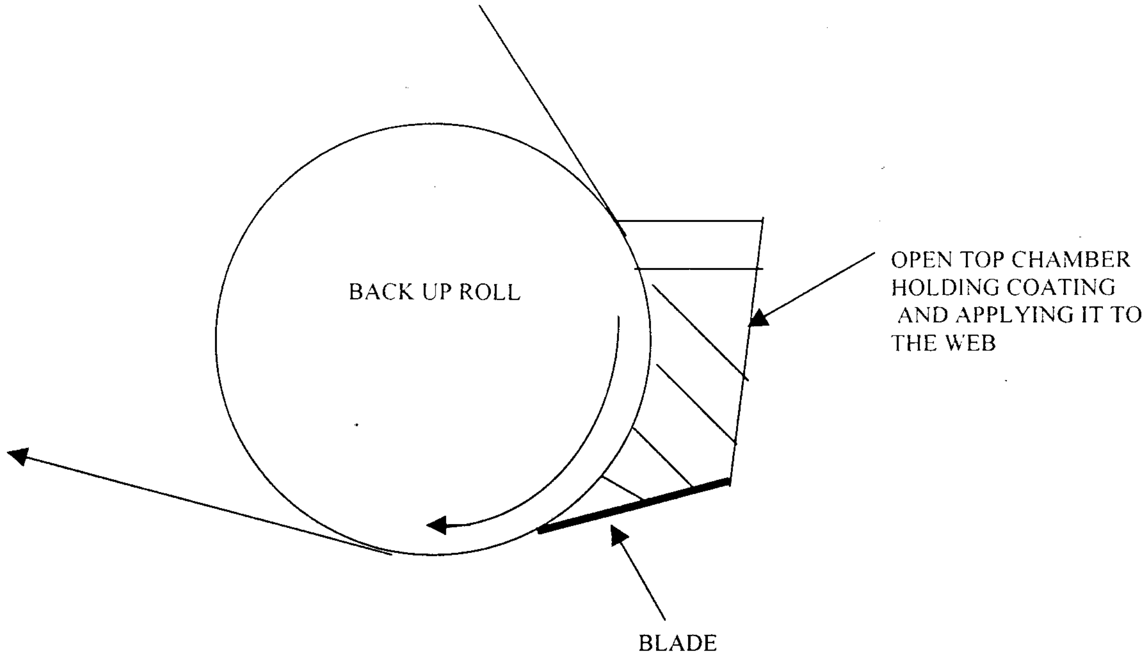

FIG. 5: POND OR PUDDLE TYPE BLADE COATER

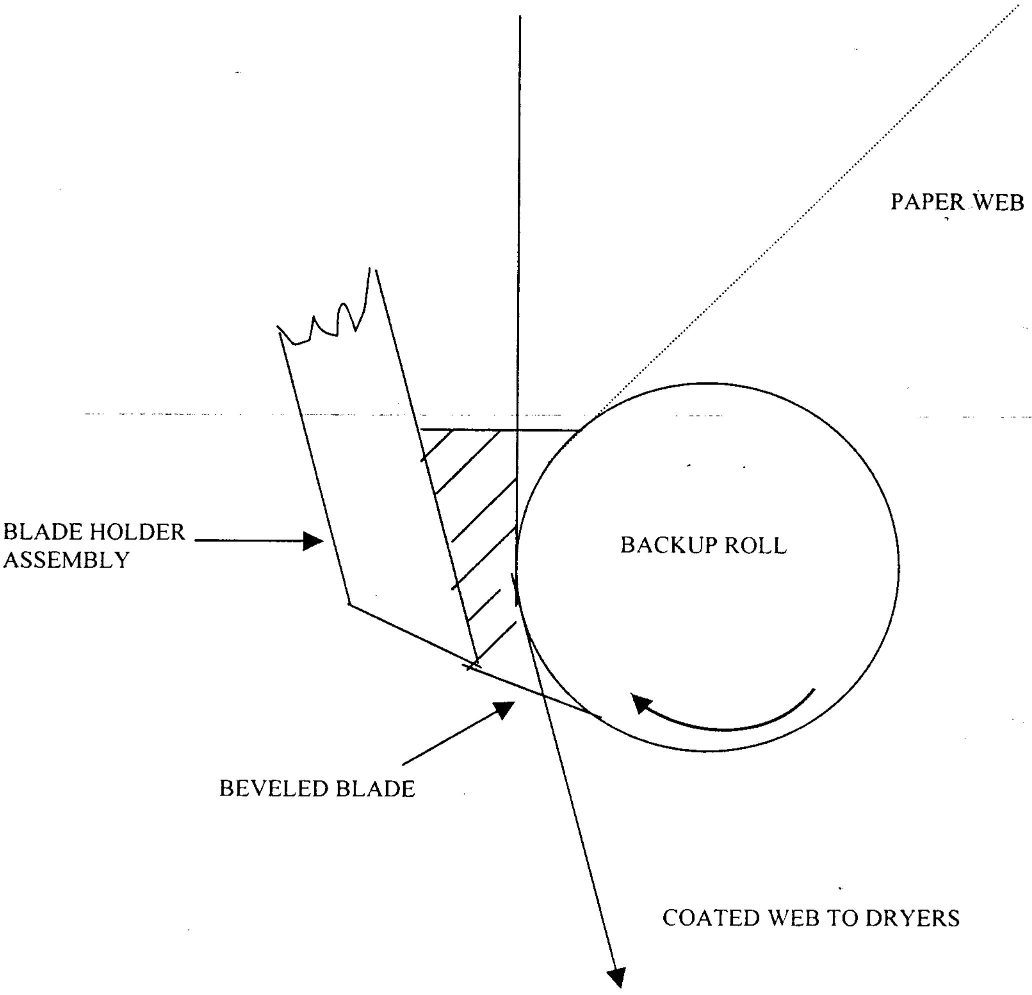
PAPER WEB
BLADE HOLDER ASSEMBLY
BACKUP ROLL
BEVELED BLADE
COATED WEB TO DRYERS

FIG . 6

THE COATING MACHINES — BLADE AND AIR KNIFE COATER

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Has around 5 years experience in a Paper mill in the area of Stock Preparation and Paper Machine. He is also an active member of CPPRI's Energy Audit team. Recently he has undergone training in the area of Stickies removal from *CTP France*, one of the leading organization actively persuing research in Stickies removal technology.

THE COATING MACHINES—BLADE AND AIR KNIFE COATER

Sanjay Tyagi

1.0 INTRODUCTION

Paper and board is pigment coated to achieve an even, smooth and uniform surface. The porosity of the coating on the surface prevents the printing ink from penetrating into the fiber structure. The typical thickness of the coating is in the range of 5 to 20 μm, which is equivalent to a coat weight of 5–20 g/m^2 per side. Paper is coated by applying coating in a coating station, and then drying it to evaporate excess water and set the binders. A coating station and drying can be incorporated in a paper machine (on-line) or installed with a separable coating machine (off-line). For applying the coating color to base paper, we need two steps

1. Application of coating to cover every spot on the paper;
2. Metering of the coating to a desired coat weight.

To fulfill these two essential functions, a coater station comprises an applicator head and a metering element. Based on the metering of the coating, the coating technology can be divided into three types—Blade, Rod, and Air-knife.

The two most popular means of applying coating to a web of paper are with the applicator roll system and with the short dwell coater. With both systems, either uses a bent blade or rigid leveled blade to meter the excess coating from the paper web. Other coating application systems are puddle coater, BTG Billblade coater and fountain coater. In this topic, we will discuss various coating application systems and metering them.

2.0 FLOODED NIP AND SHORT DWELL COATERS

The flooded nip coater, or applicator roll coater, as commonly called is designed for the application of wide range of coat weights either on or off machine. The term "flooded nip" is derived from the nip formed between the applicator roll and the backing roll which is flooded with coating to develop a hydraulic pressure (**Fig. 1**). The applicator roll rotates in a pan of coating and applies an excess of coating to the paper web as it passes through the nip formed by the applicator roll and the backing roll which supports the sheet. The hydraulic pressure in the nip eliminates slip coating caused by foam. Bubbles that form are immediately collapsed. The pressure promotes good adhesion of the coating to the paper web. The excess coating is removed with an inverted trailing blade.

An excess amount of coating is supplied to the pan and is allowed to overflow into the return compartment. The coating is introduced to the pan through a header pipe and series of small inlet tubes. Dial indicating micrometer stops with screw jacks allow precise adjustment of the gap between the backing roll and applicator roll. The wide gap lowers the amount of coating forced into the sheet. This nip gap has a range of operation of 0.127-0.178 mm, normally. The applicator roll speed is adjusted from 10% to 35% of the coating line speed. Both the speed of the applicator roll and nip gap can be varied to control the amount and characteristics of the coating applied.

3.0 SHORT DWELL COATER

The term "short dwell" refers to the relatively short period of time. The coating is in contact with the sheet before a trailing blade meters off the excess. The short dwell coater consists of a captive pond just prior to the blade (**Fig. 2**). The pond is approximately 6.35 cm. in length and is slightly pressurized to promote adhesion of the coating to the paper web.

The excess coating is channeled over a deflector and collected in a return pan before returning to tanks to be screened. Both deflector and return pan are jacketed to accept a chill water to promote sweating, making clean up easier.

Coating is supplied to the short dwell coater head using multiple inlets to ensure a uniform coating pressure across the width of the sheet. From multiple inlets, the coating enters the large cross machine chamber. Coating must then pass through either one or two orifices before entering a smaller, cross machine chamber. One orifice is a slot that the coating travels through to enter the cross-machine chamber adjacent to sheet. The orifices are required to back pressure the coating to obtain a uniform coating pressure against the sheet. The uniform pressure promotes a uniform coat weight profile.

Coating is usually supplied to the sheet dwell coater head by variable speed pumps to provide another method of affecting coating pressure against the sheet. Flow rate required is dependent on coating viscosity; baffle height, machine speed, and base sheet properties. The actual operating range is between 0.7 and 1.5 gal/min/inch width.

The main advantage offered by the short dwell coater over the applicator roll coater is reduced blade pressure required for the same coat weight. The reduced blade pressure is the result of a lower amount of coating penetration into the paper web during application with the short dwell coater. Fewer sheet breaks has been reported with short dwell operation.

4.0 COATER HEAD

The coater head is a rigid box section beam designed for minimum deflection. The blade is clamped by means of a solid clamp jaw and pneumatic tube uniformly along its entire length to ensure a uniform blade load resulting in a more uniform coat weight profile. The blade clamp and blade holder are solid stainless steel.

During a blade change, the clamp opens slightly allowing the blade to be removed and new one installed without opening the chamber so no coating is lost.

5.0 METERING OF THE COATING

After the sheet exits the coating application nip, it comes into contact with metering blade. The blade material is usually blue steel and blade thickness ranges from 0.35 mm to 0.635 mm blade width for leveled-blade operation ranges from 7 cm to 8.9 cm.

A leveled blade has a pre-honed angle, which is precisely ground by the manufacturer. Typical level angles range from 30° to 50°.
The blade forms a nip with the backing roll, which the sheet must pass through. As the sheet passes through this nip, excess coating is metered off by the blade to the correct amount. The pressure exerted on the blade determines the force at the blade nip and the amount of coating that will be metered off, thus controlling the coat weight. Profiling screens are also provided on some coaters which allow operator to adjust blade pressure every 4–6″ to compensate for base paper variation.

An alternate to leveled blade is to use a bent blade as the metering element. This blade is approx. 12.7 mm wider than leveled blade, and the sheet runs on the flat of the blade itself (**Fig. 3**). A bent blade may be used in the production of coated board where a high coat weight is required at relatively slow operating speeds.

Another reason of using bent blade rather than a leveled blade is to reduce coating scratches caused by contamination in the coating. A bent blade is less prone to contamination-caused scratches than a leveled-blade system.
An alternate to the use of a blade to meter the coating is the use of rotating steel rod. The steel is supported in polymeric holder, which is positioned in the blade holder in place of blade (**Fig. 4**). The rod holder usually includes channels for circulation of water to keep the rod clean. The rod is normally driven by variable speed motor.

Rods are used in the production of coated board where coating scratches are a problem due to particle lodging under the blade. Rods are also used in coated paper production when contaminants in the paper lodge the blade and came coating scratches.

6.0 TIP ANGLE CONTROL

“Blade tip angle” is the angle formed by the tangent lines of the backing roll and the blade and is controlled by the position of the blade beam. (**Fig. 5**). Ideally, once a coating station is set up and the coated quality is good, the tip angle should not be changed. However, on production coaters, tip angle does change with change in blade pressure. Blade pressure will change during the production run as the automatic coat weight control system makes pressure adjustments to maintain target coat weight.

Due to importance of tip angle in controlling coat weight and coated sheet quality, most new coating stations are now equipped with devices that automatically control the blade beam in response to a change in blade loading takes place automatically.

7.0 PUDDLE TYPE APPLICATOR

In puddle type applicator, puddle of coating is formed by the backing roll (covered by the web), the blade and blade holder and the front wall of the coating head. (**Fig 6**). The edges of the puddle are formed by dams that contact the backup roll. The depth of the puddle is adjustable.

8.0 FOUNTAIN APPLICATION

In this application (**Fig 7**) the coating is pumped through a slot, aimed upward toward the web and backup roll creating a fountain of coating. The paper wrapped backup roll is positioned at an adjustable distance from the lip of the slot. The slot lips can tilt, so the entering opening is large than the exiting opening. This pre-meters the coating before the blade.

The fountain water experienced problems in eliminating large air buffles and did not provide equal application pressure across the slot. This results in both slip coating and non-uniform coat weight application.

The small space requirement of the fountain allows the designer the flexibility to position the fountain very near the blade or far away from it, thus creating a variable-dwell time applicator.

9.0 AIR KNIFE COATERS

The air knife coater (also called air doctor, air blade or air brush) is another most commonly used coater. In air knife coater (**Fig 8**), the web coming from the unwind passes over a guide roll and a feed roll directly to the coating applicator roll. It then passes to the breast roll with the dip roll depressed. Excess coating weight was picked up on the paper and removed by the air stream as the web passed round the breast roll.

Air knives are the metering devices used to reduce an excess of applied coating material on moving web to a uniform thickness. There are two types of air knife operating methods. (a) Air brushing- where a gentle jet of low velocity, impinging on a vertical running coated substrate at approximately a right angle, providing a pressure dam which limits the amount of coating liquid passing by. Excess liquid runs back down the strip under the influence of gravity to a pond or drip off point. (b) Air knifing – where a jet of moderate to high velocity air impinges on a coated substrate supported by a roll, at an angle on the order of 45 opposed to substrate movement. The jet shears the liquid film, and removes the excess as liquid, spray or mist. This excess is then collected in a blow off containment system.

10.0 FILTER CAKE THEORY

The theory in removal of excess coating by the air doctor is called the filter cake theory. A coating is applied in excess to the sheet at the applicator section. Water is the coating immediately begins to migrate at the interface of the wet coating and paper web so that the coating at this point immediately becomes semidry or plastic. As the sheet of the paper passes under the air knife jet, the fluid coating is removed from the sheet by the air doctor and is sheared at the point where the filter cake begins. There is a zone in the coating cross section where the coating makes the transition from the fluid to a semi-plastic coating, and it is in this area that the air doctor shearing takes place.

The exact point at which the shear takes place varies with the amount of energy that the air blast has. At a very high pressure or velocity of air from air doctor, the air penetrates more into the filter cake or plastic area, leaving less coating on the sheet.

11.0 COATING APPLICATION SYSTEM

There are many systems through which coating slurry can be applied to the base paper. Presently three systems are mainly used. (1) Single roll system, (ii) Two roll system and (iii) Three roll system (**Fig 9**).

11.1 Single Roll System

It is a single roll normally rotating in web direction at a speed of 10 –40% of the web speed, which picks up a crudely controlled amount of coating and applies it in excess to the web that wraps the roll. The runback of coating should be laminar in nature and not a cascading effect in order to get a smooth application of coating to the web and to prevent foam generation caused by turbulent flow and cascading of the coating off the roll. This system is simplest available and used by vast majority of air knife coaters in operation and is used almost exclusively at speeds below 250 m/min.

11.2 Two Roll System

The two-roll system provides an additional metering nip to reduce and level the amount of coating applied to the web. Ti is generally used for moderately high-speed wide machines running over 200 m/min speed or at a width greater than 3.8 mts.

11.3 Three Roll System

The three-roll system was developed for high speed air knifing (over 600 m/min) to further reduce and even the coating applied to the web. The air knife is generally limited to pressure below 62.1 kPa, which limits the amount of coating which can be metered off at high speeds.

12.0 AIR KNIFE METERING ELEMENT

There are numerous designs of knives used as metering elements. The elements of adjustment and control of air knife include the slot opening g of the lips and the relationship of the top and bottom blade tips. i.e. the amount of overhang of the top lip relative to the bottom lip.

Modern air knives have very good adjustments to maintain the slot with one lip always fixed in position. Most knives use a push pull arrangement to "wrap" the adjustable lip and maintain a uniform slot regardless of air knife length. Operation slot opening ranges from 0.020 in. to 0.008 in.

The overhang or relative position of top lip to the bottom lip is important in asymmetrical lip designs. The top lip usually will extend 0.005 in. to 0.008 in. beyond the bottom lip. This gives some stability to the fluid stream and directs the stream downward from the bisector of the angle formed by the lips (**Fig 10**).

12.1 Air Delivery System

The air delivery system of a coater consists of four basic elements.

1. The blower
2. After cooler
3. The pipings
4. Means of adjusting pressure and flow.

12.1.1 Blowers

The blowers for an air knife should always be a centrifugal type to deliver clean air, free of water and oil and completely free of pulsation. A blower should be sized according to the cubic feet/minute (CFM) required at the largest gap setting and highest pressure required. Allowance should be made for pressure drop through the piping system and after cooler. Air volume requirements vary with air knife length, air knife gap and pressure requirements.

12.1.2 After cooler

Air temperature increases roughly by 16 F for each pound of pressure increases. Generally after coolers are installed for system operating over 24kPa. There are two methods of cooling the blower air. Water-cooled heat exchangers and water-injection systems. Water-cooled heat exchanger system is commonly used. The air is cooled without contacting the cooling water. Water injection systems cools by injecting a small amount of water mist into air stream. The air is cooled by the massive heat absorbed as water evaporates. The drawback of this method is that any impurities in the water remain in the air stream.

12.1.3 The piping

The general rule with piping system is to keep them as short as possible with no sharp bands. To keep pressure loss to a minimum, piping from the blower should be at least 20% larger than the inside diameter of the blower outlet, until it splits off to each end of the air knife. The tee should be the same size as the main supply line and made of hard pipe. Flexible hose at each end of the air knife should be sized for flow equivalency.

12.1.4 Pressure and flow adjustments

Blowers can be throttled to adjust the discharge pressure or inlet volume or both to any selected point within the operating capability of the blower. This is usually accomplished by installing and adjusting a blast gate or butterfly valve on the inlet or discharge opening of the blower.

When throttled at discharge, the throttling device will supply sufficient resistance to air flow to provide the desired effective overall discharge pressure beyond the throttling device as required by the process.

Another method of pressure and flow variation is by varying the speed of the blower motor. This method is most energy efficient method. The volume entering the blower varies directly with the speed in rpm, but the input hp varies with the cube of the speed in rpm. Fairly large energy saving can be made by this method. Another advantage of variable speed control is that it lowers the output temperature of the blower in comparison to the other two methods.

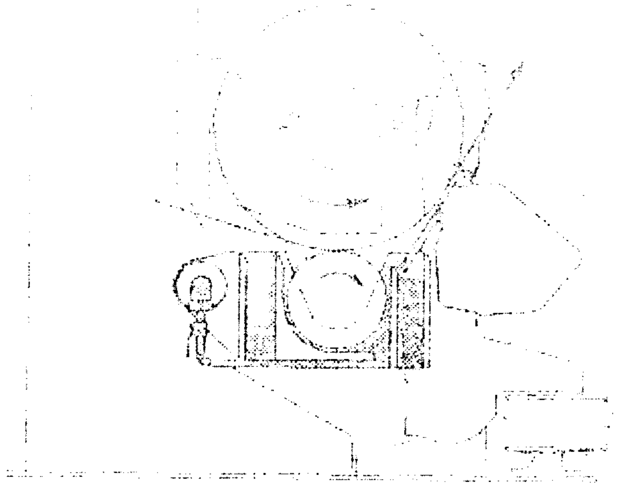


FIG. 1: FLOODED NIP COATER

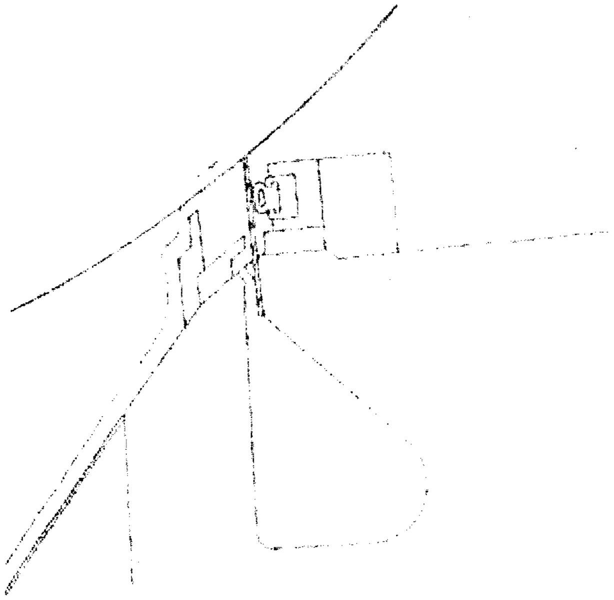


FIG. 2: SHORT-DWELL COATER

FIG. 3: BENT-BLADE COATER

FIG.4: ROD METERING

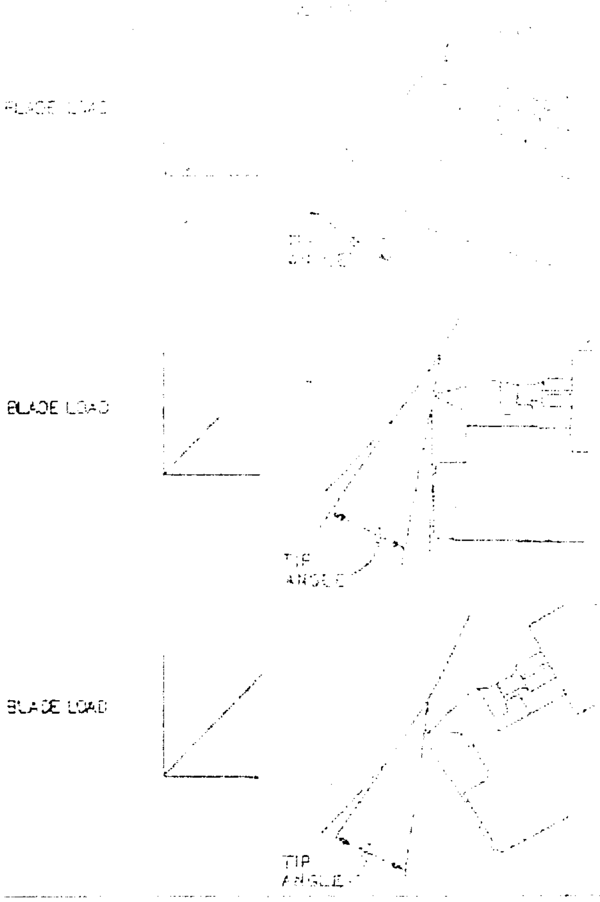


FIG. 5: BLADE LOADING AND TIP ANGLE

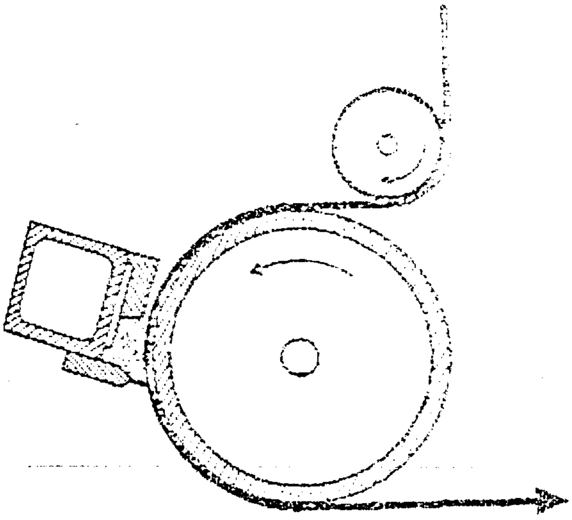


FIG. 6: PUDDLE COATER

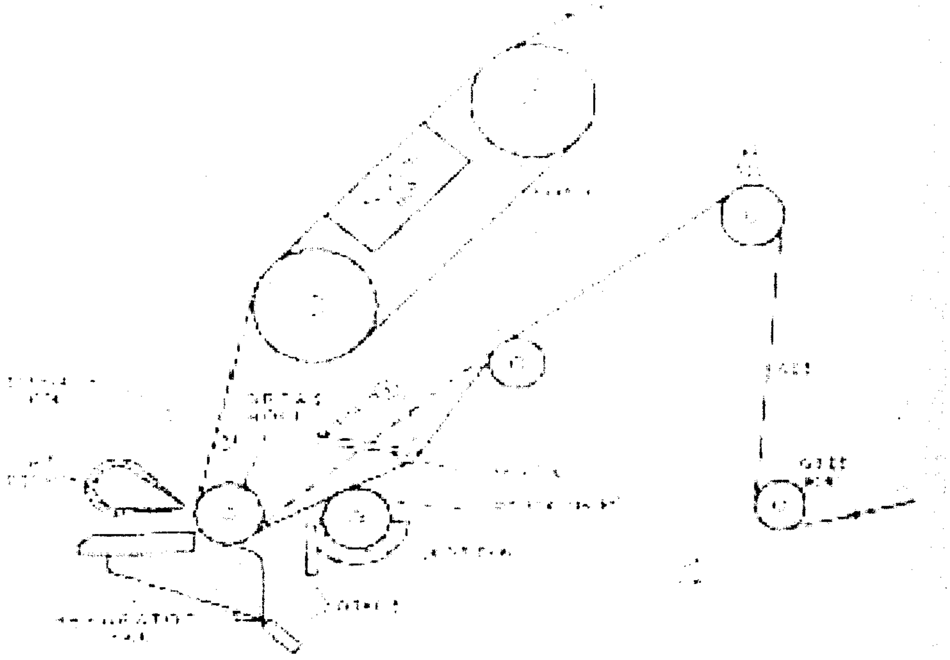


FIG. 8: AIR KNIFE (DOCTOR) COATER

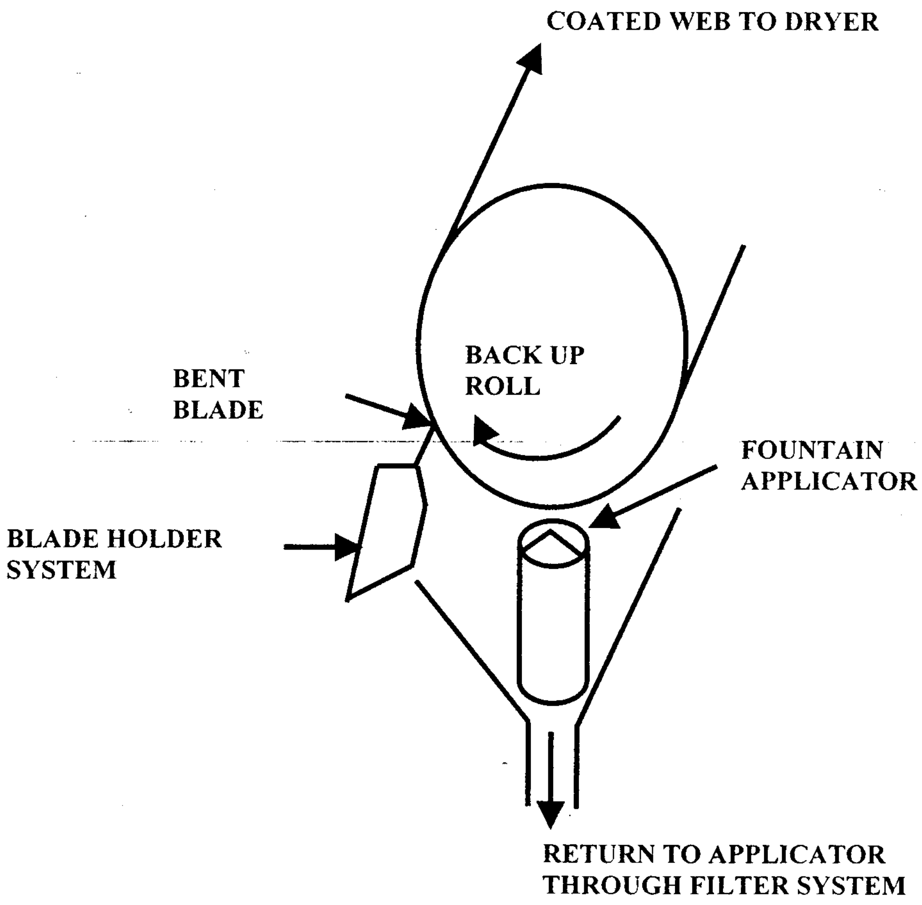
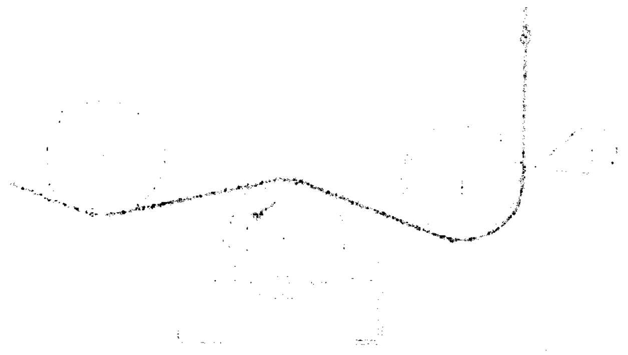
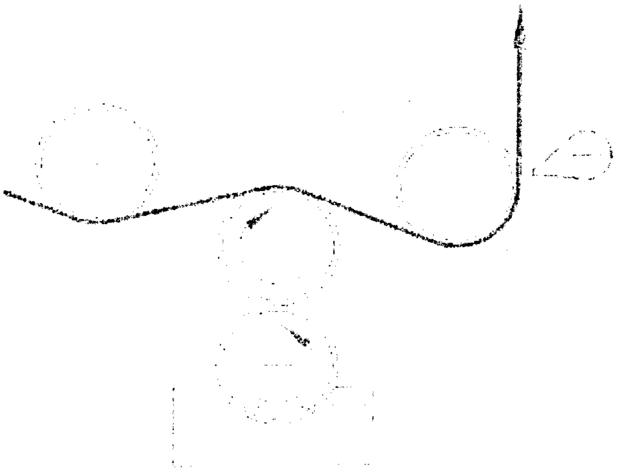


FIG.7: BLADE COATER BENT BLADE WITH FOUNTAIN APPLICATOR



Single roll



Two roll

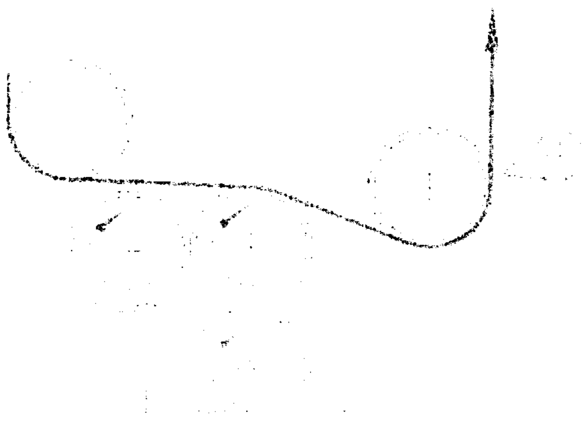
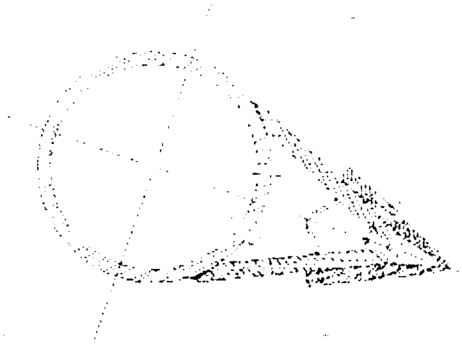
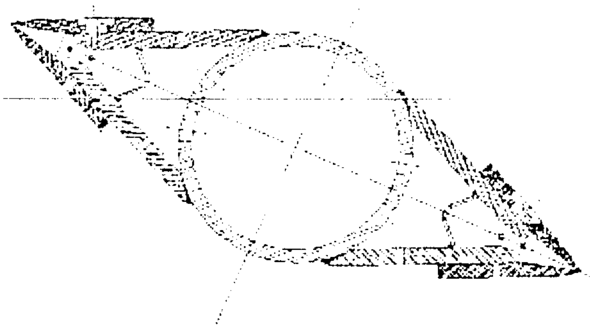


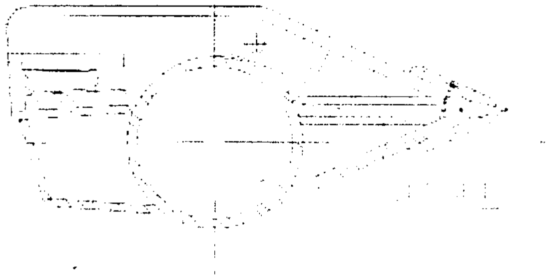
FIG. 9: AIR KNIFE APPLICATOR

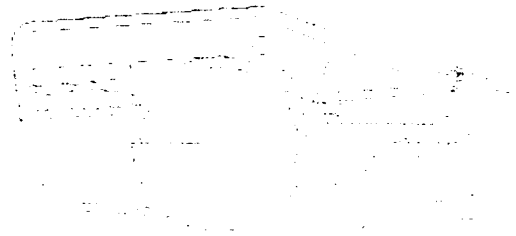


Non-opening airknife



Dual rotating airknife





Opening airknife

FIG. 10: AIR KNIFE METERING ELEMENTS

SURFACE STRENGTH OF COATED PAPER. COMMON PRINTING DEFECTS AND THEIR REMEDIES

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SURFACE STRENGTH OF COATED PAPER. COMMON PRINTING DEFECTS AND THEIR REMEDIES

Y.V. Sood

1.0 INTRODUCTION

Surface strength is an important requirement for coated paper to be used for offset and lithographic printing. Picking is the rupture of the surface of paper or board during printing which occurs when the external tensile force applied to the surface is greater than the cohesion of the paper or board. When ink is applied to paper under pressure, considerable force is exerted on the paper surface when the ink film splits. If the cohesive force, or resistance to splitting, of the ink is greater than that of paper, then the split takes place in the paper rather than in the ink. The magnitude of the force is dependent on the speed of printing and the tack of ink.

Coated papers have a mineral layer attached to the base sheet by means of an adhesive. The pick resistance describes the ease of removal of this coating. A high pick resistance is desirable since this will permit the use of high printing speeds and concentrated inks.

2.0 IMPORTANCE OF SURFACE STRENGTH FOR DIFFERENT PRINTING PROCESSES

Picking is not a defect of the gravure process, since the force exerted by the low viscosity, solvent-based inks is small. Loose fibers can, however, cause trouble by lodging under the doctor blade, where they wipe out of the cells, causing white streaks on the print.

Picking is more serious in ~~litho than~~ letterpress for the following reasons:

Ink is applied in thin films from a flat surface, and has to split twice, from plate to blanket, and from blanket to paper. The ink must be of high tinctorial strength if saturated colours are to be obtained, and must therefore be highly pigmented. It must have extremely good flow properties to maintain uniformity in very thin films, and good flow properties in conjunction with high pigmentation means that on the whole offset inks must have rather higher viscosity and tack than letterpress inks. Thus when ink film splits more force is exerted on the paper surface, so a stronger surface is required to prevent rupture.

A further point to note is that because of the tack of the ink, the sheet tends to follow the blanket before being peeled off by tug of the grippers. The tackier the ink the more this occurs, and therefore the greater the angle through which the paper is bent as it is peeled off. This bending is sufficient to crack the coating, and further increases picking.

Clearly a more rigid paper will be able to follow blanket less than a less rigid one. Thus picking can be minimized by using a more rigid paper. This rigidity effect is believed to be the reason why picking is always less in the machine direction than in the cross direction.
On two-colour offset machines, the second colour is applied to areas of the sheet that have been damped a second or two previously, during application of the first colour. If the coating is water sensitive, it will be dampened by this damping, picking occurring on the second colour although the ink tack is less. Surface strength must therefore be higher initially to compensate for this effect, and coatings must not swell in water. Second unit picking occurs mostly on starch coated papers, but has been known on casein coating when the casein has been insufficiently hardened.

Apart from large scale picking, if the coating is partially soluble, coating ingredients may build up on the blanket and abrade the plate, or contaminate the fountain solution, causing various scumming and tinting effects. Minute quantities of soluble casein are particularly prone to cause scumming troubles.

3.0 DEFECTS

Pieces of the paper surface will be pulled out during printing on papers of poor picking resistance, especially if the inks are tacky or the press is run at high speed. The appearance of white spots on image areas and 'hickies' secondary pick marks with white holes) are symptomatic of the defect. It is usually more prevalent at the leave edge of the forme or plate where the pull at parting is greater.

Irregularities in the surface of the stock may often be responsible for the onset of picking on the press run. Wrinkles in coated papers, undigested fibre clumps, contraries in a lined board, are typical causes of spotty picking, while on the other parts of the sheet the pick resistance may be good. This type of picking may be the most difficult to assess by a printability test unless selective sampling is carried out and the pick test made on a suspect portion of the sheet. Minute picking on coated stocks and imitation arts is also often difficult to detect unless a microscope is used. If the inking rollers are not scavenging the forme well minute particles may remain on the forme and be battered or punched into the plates on a letterpress machine.

Picking can also cause wear and scumming of litho plates. The picked off material may act as an abrasive, with the result the plate image may "blind". The opposite effect, scumming. is also possible, since if the abrasion removes the hydrophilic layer on the plate, the exposed portion may accept ink and scumming develop.

Scumming may also result if the picked material is a coating containing water soluble casein. Now that the use of wet on wet multi-colour printing is increasing on coated stocks for quality litho work, the moisture susceptibility of the coated surface is increasingly important.

4.0 METHODS OF TESTING SURFACE STRENGTH OF PAPER

Two tests are in general use:

1. Dennison Wax	Tack graded waxes
2. IGT	Laboratory Printing Unit

4.1 Dennison wax

The waxes used in this test are tack graded. The end of a wax is melted in a spirit flame, and pressed firmly onto the paper sample. After 15 min. it is pulled away, the tip of the wax and the paper being examined for picks, breaks or blisters. The adhesive power of the waxes increases with ascending wax number. The result is given as the highest number on which no disturbance of the surface takes place. This test produces reliable results on papers that contain only starch or casein as coating binders. It can be misleading on modern papers, which often includes latex or synthetic binders in the coating formulation. The hot waxes are liable to melt the latex, giving low results on papers that do not pick during printing. Conversely, the waxes fail to key on some synthetic resins and can give high results on poor papers.

Bearing these limitations in mind, a coated paper showing no pick with a No. 6 wax would normally be satisfactory for offset litho printing. Liner boards should not delaminate below No. 10.

4.2 IGT printability tester

Basically this tester is a small printing unit. A print can be made between 10 and 32 mm wide (depending on the model) by 200 mm long under controlled pressure and ink film thickness, at gradually increasing speed.

It has been shown that, with a Newtonian oil, pick can be measured by the product viscosity of the oil x printing speed. If then an oil of known viscosity is used for printing, picking will be determined by the speed of printing.

The printed strips are examined under a special pick view starter instrument to determine the position at which the first signs of surface disruption occur. By measuring the distance from the start of printing to this point, the critical speed can be found by reference to a calibration curve.

This test correlates well with the behavior of paper during printing. As a guide, for lithographic printing the paper should not show any pick up to viscosity velocity product (VVP) of 108 Poise·m/s using IGT viscosity oil at 27°C and 65% RH. However in letterpress work little trouble is generally experienced with papers showing no pick up to VVP value of 72 Poise·m/s.

With inks and ink vehicles that show complex flow properties, the viscosity/viscosity relationship does not hold. The significant ink property is then not viscosity but tack strength, which can be measured on a Tackmeter. A series of tack-graded inks can be obtained, and used for this test in place of IGT oils.

5.0 FLUFFING TENDENCY

Another aspect of surface strength is fluff tendency. This is the release of fluff, or dust, consisting mainly of individual fibers or particles of loading, or very small aggregates of these materials, from uncoated paper surfaces during the printing process.

If these fibers or particles have been created during cutting and slitting operations the effect will be the same, but the defect cannot be classified as due to poor surface strength.

Thus fluffing can be due to cutter dust, or due to some fibers in an uncoated paper surface that are insufficiently bonded to their neighbors, whereas picking is a reflection of the total surface strength of coated papers.

In letterpress, the paper contacts the frame in the printing area only, *whereas in offset there is overall contact between blanket and paper.* The deformation of the blanket in the nip also exerts on the paper a force sufficient to remove loosely bound fibres.

These disrupted particles adhere to the rubber blanket. Moreover, the fibers, being hydrophilic, accept water in preference to ink, so one particle will print a white blob for many hundreds of sheets before it inks over. In letterpress the particles are removed about on the forme by the inking rolls and, since there is no water present, ink over much more rapidly and do not blemish the print.

Fluffing is the most troublesome in offset lithography, where the material from the paper builds up on the blanket, compelling frequent wash-ups.

Print quality degradation takes many forms:

1. The fluff accepts water rather than ink, causing white fibrous marks on solids
2. Halftones fill in, causing poor definition and loss of contrast

3. Ink transfer is impaired. As fluff builds up on the blanket the colour gradually lightens. After a wash-up, colour returns to normal. Thus it is impossible to maintain consistent colour throughout the run.
4. The deposit on the blanket may wear the plate, particularly if it contains abrasive materials such as china clay.
5. If there is sufficient fluff to be fed back into the ink, the ink becomes stodgy and flow properties are impaired.
6. On boards, trouble often arises from the backs, more often on MG boards where these are of rough mechanical wood. The tacky ink of the first colour will pull fibers from the back of the board above it in the stack, feeding these fibers back onto the blanket when printing the second colour.

The rubbing action in the feeder is also sufficient to loosen fibers from these weak backs.

6.0 FLUFF TESTERS

Fluff tests available can be classified into four main types:

1. Vacuum application: *FOGRA, Munich, IGT, Leipzig*
2. Application of a tacky material: *Papirindustrens Forskningsinstitut, Norway; IGT, Amsterdam*
3. Light rubbing or abrasion: *Pira; IGT, Amsterdam*
4. Fibre rising tester*: Fibro, FRT Sweden.*

Fluff troubles can be divided into three main types:

1. Completely loose material arising from cutting and slitting operations.
2. Paper of very low general and surface strength
3. A well-formed sheet of good general strength, but containing a limited number of fibers insufficiently bonded into the sheet, which are released during printing.

6.2 Vacuum application

Tests of this kind only appear to pick up completely loose material from the paper, unless the vacuum head is in contact with the paper, applying a rubbing action. It was not found possible to control this rubbing action sufficiently to make the test reliable.

6.3 Application of a tacky material

This kind of test applying a tacky material is a pick test rather than a fluff test. A major difficulty in this sort of testing is to obtain a tacky strip, which remains at the same degree of tackiness. The Norwegian test, which uses coated film material of the kind used for taking fingerprints, is said to work on boards, but removes the surface from papers.

6.4 Light rubbing or abrasion

IGT produced a test in which an endless belt of paper was run rapidly round a series of knurled rolls, the resulting fluff being collected on tacky glass slides. The paper strip was only one inch wide, so that there was a very large effect. We were only able to produce fluff on this test from papers such as newsprint. Strong papers, such as cartridge did not fluff on this test.

When paper is fed through a nip in contact with a rubber blanket, the blanket distorts, applying a light rubbing action. This is the principal of the PATRA Fluff tester. Fibers removed from the paper adhere to the rubber blanket, and can be counted.

6.5 Fibre rising tester (FRT)

The fibre rising behaviour of paper sample can be evaluated using Fibre rising tester (FRT). In this device a paper surface is moistened and dried under controlled conditions simulating the printing press. The fibres lifted off the surface while passing over a sharp lined edge are imaged with oblique lightning and images are counted as long and short fiber components.

7.0 COMMON PRINTING FAULTS, THEIR CAUSE AND REMEDY

Faults will develop if the paper properties important for printing are incorrect. These properties can be divided into the following main areas:

- Smoothness
- Absorbency
- Surface strength
- Water susceptibility
- Chemical

Optical properties are important, but are common to all printing processes.

7.1 Smoothness

This is an obvious factor in the production of good quality print. The smoother the surface, the greater the number of lines per cm of the screen ruling of half tones which can be used. The rougher the surface, the more ink has to be applied in order to ***bottom*** the irregularities in the sheet, and the heavier the impression pressure that has to be used.

While a smoother paper will always have the potentiality of producing a better print, this requirement is not critical in offset lithography because the resilient rubber blanket is able to accommodate to rougher stocks.

Faults due to roughness are rare in offset lithography. However, faults have been known to arise on very smooth, glossy coated papers, due to good overall contact between the blanket and the paper. Delivery troubles have occurred due to the difficulty of peeling the paper away from the blanket, even in non image areas.

7.2 Absorbency

The absorbency of the stock is important in controlling several aspects of print quality.

a.	**Defect**	SET-OFF
	Appearance	White spots on printed areas. Spots of ink on back of

		sheets
	Cause	Low absorbency. Ink vehicle is unable to penetrate fast enough for quick setting
	Remedy	More absorbent paper Faster setting ink. Minimum ink film thickness Anti set off spray
b.	**Defect**	**LOW GLOSS OF INK OR VARNISH**
	Appearance	Low gloss
	Cause	High absorbency. Vehicle penetrates too rapidly
	Remedy	Less absorbent paper Faster drying ink or varnish
c.	**Defect**	**STRIKE-THROUGH**
	Appearance	Print on one side visible on reverse
	Cause	Paper opacity too low. Effect increased by penetration of ink vehicle due to high absorbency of paper.
	Remedy	More opaque, less absorbent paper Faster drying ink Keep printing pressure and ink film thickness to a minimum.
d.	**Defect**	**POWDERING OR CHALKING**
	Appearance	Ink pigment can be rubbed off surface
	Cause	High absorbency of coated paper. Vehicle penetrates leaving unbound pigment on surface
	Remedy	Less absorbent paper Faster drying ink Minimum impression pressure
e.	**Defect**	**POOR ADHESION OF BRONZE POWDER**
	Appearance	Bronze powder readily rubbed off
	Cause	High absorbency of paper. Bronze preparation adsorbed too rapidly
	Remedy	Paper of low absorbency
f.	**Defect**	**MOTTLE**
	Appearance	Uneven, streaky or spotty gloss of colour variations
	Cause	Papers with hard spots; heavy wire marks; badly surface sized.
	Remedy	Change paper.

7.3 Surface strength

Two major properties come under this heading — PICK RESISTANCE and FLUFF TENDENCY.

a.	**Defect**	**PICKING (COATED PAPERS)**
	Appearance	Irregular white areas, where paper surface has been torn away
	Cause	Ink tack too high for surface strength
	Remedy	Reduce ink tack (can cause other defects) Change to stronger or stiffer paper. Reduce printing speed
b.	**Defect**	**SECONDARY PICK OR HICKY**
	Appearance	Inked spot surrounded by unprinted halo registers from sheet to sheet
	Cause	Particles of foreign matter on blanket e.g. particles picked from paper, cutter or guillotine dust, ink skin etc.
	Remedy	Stop press and clean blanket Identify particles, and remove surface of contamination
c.	**Defect**	**FLUFFING (UNCOATED PAPERS)**
	Appearance	1. White fibrous tracks or spots in printing areas 2. Loss of contrast 3. Filling in of half tones 4. Colour variation
	Cause	Loosely bound fibers and loading material coming away from the sheet. Cutter or guillotine dust on surface Fibers from damper rolls
	Remedy	Stop press and press blanket (short-term remedy, as deposit will build up again) Change to less fluffy paper Keep impression pressure to minimum

Fluffing and picking offer good illustrations of the interdependence of factors. These defects cause deposits on the offset blanket, which can cause wear on the plate, particularly if there are abrasive loading materials in the deposit. Thus, paper defects can give rise to plate defects, although the paper never contacts the plate.

7.4 Water susceptibility

a.	**Defect**	**WET PICK (COATED PAPERS)**
	Appearance	As for picking. Occurs on second or subsequent units of multi colour presses
	Cause	Water swellable coatings, the pick strengths of which are reduced by the damping water.
	Remedy	Stop press and clean blanket Reduce damping to a minimum Use alcohol in fountain solution Change paper
b.	**Defect**	**CASEIN SCUMMING (COATED PAPERS)**
	Appearance	A tint on non-printing areas, increasing in intensity with number of sheets fed. Usually on second and subsequent units of multi-colour presses.
	Cause	Soluble casein from the paper coating dissolving in the damping water and sensitizing the plate
	Remedy	Cut water to a minimum Use alcohol in the fountain Use Epsom salts in fountain solution Make sure fountain solution is between pH 5 and 7 Leave paper for some weeks to harden Change paper.

7.5. Chemical

Casein scumming could be classified as a chemical effect, as the casein reacts to sensitize the non-image areas of the plate to ink.

As the paper does not contact plate, it can contain materials that may react with the plate provided that these materials stay in paper, and do not either fluff out of it or dissolve in the damping water. Materials can only harm the plate if they are able to contact it, either via the blanket or the damping water.

The major chemical fault that can arise from paper is due to acidity

a.	**Fault**	**DELAYED INK DRYING**
	Appearance	Ink remains liquid for a long period, smearing when rubbed
	Cause	Paper with pH below 5, in conjunction with high humidity Oxidation drying is delayed
	Remedy	Change paper

This effect is more common in offset lithography than other printing processes. Even if the atmosphere is not particularly damp, the RH in the printed stock can rise sufficiently due to damping water applied when a number of colours are printed.

b. Excessive quantities of chlorides in paper can cause plate corrosion (>0.5%)

There are a number of faults that may develop due to ink and its reactions with other factors aside from paper.

a.	**Fault**	**NON-TRAPPING (WET-ON-WET)**
	Appearance	Second or subsequent colours do not trap on these put down previously
	Cause	Wrong track sequence. The first colour down should have the highest tack and subsequent colours should be tack graded
	Remedy	Obtain ink set correctly tack graded
b.	**Fault**	**INK TINTING**
	Appearance	A tint on the non-printing areas that can be removed from the plate by washing with water. Under magnification it appears as individual droplets
	Cause	Ink emulsification in the fountain solution
	Remedy	Stiffen up the ink Check that the fountain solution is not alkaline, lower pH if it is Change ink

A similar fault may occur if the ink is unsuitable for lithography and the ink pigment bleeds into the water, but this is quite rare.

PERFORMANCE OF DIFFERENT STARCHES AS COATING BINDER

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PERFORMANCE OF DIFFERENT STARCHES AS COATING BINDER

A.K. Ray

Extended Abstract

Starch is the most commonly used surface sizing and coating agent of the order of around 60 of binder requirements. For surface sizing a relatively low viscosity solution of 3 to 9% solids is used at the size press to achieve pickup in the range of 30-50 kg of dry starch per tonne of paper produced. Starch is supplied as a white granular powder, which is insoluble in cold water. On heating the water is able to penetrate the starch globules and causes them to swell, producing a gelatinized solution or paste, depending on concentration. Further cooking cause the solution to thin to a lower viscosity. Cooling this hot solution causes thickening, which is called "setback" or retrogradation. Although gelling starches have good film forming properties and thus contribute to greater surface sizing/ coating efficiency, but their high viscosity and setback causes difficulties in their application on to the paper surface. Other advantages of starch are: it does not impart color to the coating formulations, less expensive, can be used for high concentration formulations and easily dried. Due to the migration tendency of starch, it usually gives good dry pick results. Starch partly migrades into the base paper and partly into the surface of coating layer, causing a certain degree of surface sizing. Generally they have poor adhesive strength than glue or casein or any other polymeric binders like polyvinyl alcohol, and polymeric latexes such as styrene –butadiene latex, polyvinyl acetate or vinyl acetate or even CMC, sensitive to water or humidity, yield poor gloss and sometimes responsible for calender dust.

The Source of starches are: Maize, Tapioca, Wheat, Potato, Corn, Sago, Milo, Rice etc. in India; the major sources are Maize, Potato, and Tapioca. Starch is made of two long-chain molecules, around 20-30% amylose and the balance amylo-pectin. Amylose is a straight- chain molecule, white amylopectin is branched. Amylose connects at 1 and 4, as can amylopectin, but amylopectin can also branch at 6 to make a complicated molecular structure. This is the reason why cooked starch forms a gel and can be very viscous. Therefore it is essential that most of the starches used in the paper industry are required to be modified to develop certain properties in the starch so that it will be more effective and adaptive in the papermaking media by depolymerization or derivatization.

As already indicated unmodified starches differ in properties such as amylopectin-to - amylose ratio, granule dimensions, shape, gelatinization temperature, and the molecular weight of the component fractions. Some of the methods of starch modifications are:

- Physical modification methods
- Fractionation into amylose and amylopectin components

- Thermally and Thermo-mechanical conversion
- Acid modified/Hydrolysis (acid thin)
- Chemical modification
- Oxidation (oxididized by peroxide, ammonium persulphate, or alkaline sodium hypochlorite)
- Derivatization
- Enzyme conversion
- Chemically- Thermally Modification
- Genetic modification

Modified starches

Supplied modified starches can be defined as starches that the mill need only gelatinize for use. As starch is gelatinized, the adhesive character is developed. The objective of starch pasting is to separate the double helixes and dissociate the hydrogen bonds between the hydroxyl groups to maximize the amount of free hydroxyls. Once freed, it is equally important to keep the groups separated so that they are available to form bonds with other molecules such as the pigments in the coatings and the fibers of the base sheet. The adhesive character of starch is irreversibily lost if the hydroxyl groups are allowed to reassociate and retrograde. Some examples of modified starch are as follows:

1. Dextrin (Gummed labels and stamps, as well as some coatings, used to be made with these gums)
2. Acid modified starch (not having any useful viscosity properties and has low binding power)
3. Oxidized starch (Chlorinated starch with Na-hypochlorite with 8% free chlorine): Highly converted is used for clay- coating color which blends well with latexes
4. Cationic Starch (Head box and Size press, Coating); Starch-O-CH_2-CH (OH)-CH_2-^+N (CH_3) Cl^-.
5. Starch ethers or ester derivatives (with ethylene oxide or propylene oxide under alkaline conditions). Hydroxy ethylated starch (Good viscosity stability and grease resistance): Starch-O-CH_2-CH_2-OH.
6. Dialdehyde starches-DAS (obtained by per-iodic acid oxidation).
7. Carbamoylethyl starch (CES) by reacting with acrylamide in alkaline medium
8. Unmodified starch to be used as enzyme converted (bacterial alpha amylose treatment) at a pH 6.5-7.0 or thermal (no excess steam) or thermal- chemical conversion.

Dextrin (white dextrins, canary dextrins, and British gums) is prepared by treating raw starch with acid or alkali and the roasting the dry material at various temperatures from 250°F to 400 °F for various times.

Cationic starch and hydroxyethylated or hydroxypropylated starch are either chemically converted or radical substituted derivatized starch. Hydroxy ethylated or hydroxy propylated starches are normally converted in addition to being derivatized with ether linkage. These starch ethers are stable under a wide range of conditions and are compatible with most any chemical used in the paper coating and papermaking process. These starches provide significant strength improvements due to higher degree of hydrogen bonding and have improved film- forming properties over in-mill converted starches.

Cationic starches like starch ethers are less susceptible to retrogradation and are reportedly provide strength and holdout advantages superior to the other types of starches through their additional ionic forces. The majority of the cationic starch remains attached to the pigment and fiber upon repulping of coated broke. Make down of the coating color is critical due to ionic interaction. Adequate agitation power is necessary during coating make down to handle the initial high viscosity.

The oxididized starches provide increased strength and better film forming properties than acid thinned or in-mill modified starches. Highly oxidized starches retard retrogradation and can have increased dispersive powers which may or may not be detrimental to the papermaking process when returned to the furnish through the broke system.

Thermo-mechanical conversion, acid hydrolysis and enzyme conversion all lead to a decrease in the molecular weight of the starch and a corresponding decrease in the solution viscosity of starch solutions. This makes them more manageable and able to be pumped.

The most important parameters for selecting modified starches are:

The selection of starch is based on the following parameters: appearance/ form / color / texture, bulk density, pH, moisture content, acidity to phenolphthalein, packaging behavior, temperature- viscosity values, gelatinization temperature, granules size, swelling, solubility, texture, clarity, amylose content, high degree of dispersibility, binding or adhesives strength, effect on strength filler retention, high retention by wood fibers, drainability, good solubility, charge density and sign, low viscosity, no high gelatization tendency, good stability, no retrogradation tendency(setback resistance),high film forming properties, good plasticity and Low cost

They should not need extra plasticizer, must be abundantly available, should not contain undesirable components with little or no ions, should not have variable property, can be processed at high solid content, has excellent runnability in the press / film press, no or less tendency to bacterial attack (mold resistance), less temperature sensitive, flexible, less water sensitive or water absorption tendency (high water resistance), less rewetting tendency, provides rub resistance, pick resistance, rupture resistance, no tendency for linting and dusting.

Other special properties can be developed such as grease resistance, ink holdout, surface strength and fire resistance

Among the above the most important are: binding or adhesive strength, water retention capacity, rhelogy, plasticity and film forming properties

As a surface sizing chemicals starch are abundantly used for bond papers, bristols, envelope, paperboards etc. and as vegetable gums in Kraft papers. However in coating application its use alone is limited except in precoating and some other applications. However as an admixture there are plenty of applications; some of them are reproduced below:

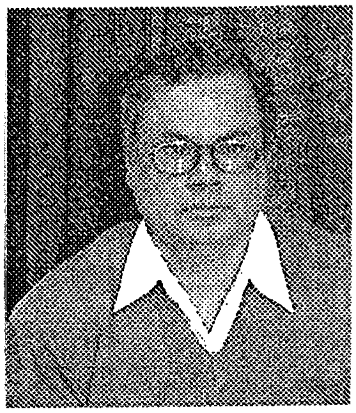
The commercial uses of starch as a coating binder or co-binder include hydroxy-ethylated starch (10%) with styrene butadiene latex 8% with clay and plastic pigment for 56.59 % solid content of coating color to achieve gloss 66, brightness 87 and opacity 95.5; for dull coat or matte finish offset paper in blade furnish P.V. acetate latex 5%, SBR latex 5% and hydroxyethylated starch 2.3% with 70% solids; for high finish SBR latex 12% and hydroxy ethylated starch 2% with also 70 % solids for supercalendered offset lithography on a sheet fed press which needs high brightness, good pick strength and stiffness etc. The amount of starch admixed with latex for clay pigmented paper has been quantified through computer program for various basis weight for offset grades where starch varies between 7- 10% and latex varies between 6-7 %, overall 14-17% requirements. The clay pigment is a mixture of delaminated and calcined clay with a coat weight 9-16%

In size press coating for sheet offset the starch can be used as hydroxy ethylated, oxidized or enzyme converted 13% with SBR latex 17% with % solids 40 at a pH of 8.5-9.5 and for size press pre-coat for sheet offset No.1 and No.2, enzyme converted starch can be used alone with solids % 25-30 for coat weight 4.5-7.5 gsm. For precoating color with solid content 55-65 % coarse $CaCO_3$ as sole pigment SB- latex 7% and starch 5 % and 0.5% Finnfix 5 (CMC) has been reported as a good formulation.

Application of oxidized potato starch – SB latex combination (6 : 6 %) with Finnifix CMC with solids content 58% having coat weight 11 gsm for LWC and offset papers.

The choice of flow modifiers and insolubilizers for starch application in coating are also discussed.

RHEOLOGICAL CHARACTERISTICS OF COATING COLOR AND THEIR EFFECT ON COATING PERFORMANCE



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RHEOLOGICAL CHARACTERISTICS OF COATING COLOR AND THEIR EFFECT ON COATING PERFORMANCE

A.K. Ray

Extended Abstract

Coated paper and board are layered construction. It is usually done to improve the printing characteristics and optical properties of paper. More explicitly pigment coating are applied to paper and paperboard in order to form a uniform, smooth, glossy and ink receptive surface on which print is to be made and to improve the general appearance of the sheet. It may provide for some special function to the paper and the finished coated paper must show an intended quality of end user.

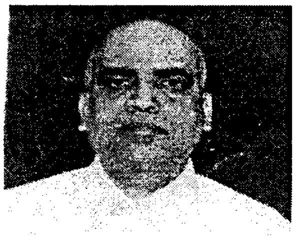
The coating color consists primarily of pigments (clay, $CaCO_3$, TiO_2, plastic pigments etc.), binder/adhesive (starches, gums, glues, casein, soya protein, polyvinyl alcohol, styrene-butadiene latex, polymer emulsions like vinyl acetate, acrylics etc.) of the level of 5-20% on the weight of pigment and small amount of large number of additives (each not exceeding 2% of the weight of pigment) in an aqueous or non-aqueous solvent. The binder is required not only to hold and bind the pigment to pigment particles, pigment to fiber, fiber to fiber together in the base sheet but also to control the acceptance of printing ink by the coating layer. The additives depending upon specific requirements includes insolubilizer formaldehyde donors as water proofing agents UF and MF resins,glyoxal) plasticizers/lubricants (soaps or Na-/NH_4 stearates , wax emulsions, sulphonated oils, esters etc.), rheology modifiers called flow modifiers/ thickeners (urea,natural polymers, CMC, etc.), dispersants (polyphosphates, lignosulphonates, silicates, polyacrylates etc.), preservatives (formaldehyde beta naphthol etc.), foam control agents- defoamers/ antifoaming agents(poly glycol etc.), dyes and colorants(direct/ acid dyes and colored pigments etc.). The materials are all suspended in a solvent generally water and the suspension is termed as coating color or coating formulation which is then applied to the surface of the paper through various types of coater. As a result a layer of coating color is formed on the paper sheet. A drying step is then followed subsequently to remove the fluid medium, water.

The properties of the final coating are therefore highly dependent on many parameters derived from individual components and maintaining consistent properties for the base paper or board, to ensure that the coating color conforms to a fixed specification. A precise quantity of coating material must be transferred almost instantaneously to the web in a form that provide uniform coverage, surface continuity and a structural configuration suitable for the intended use. Various coaters are used for the above purpose like Size press, Blade Coater, Air-Knife coater, Roll coater, Roll-Blade coater, Blade- Size press , Rod coater, differential Bill blade or Bill blade combi coater and Helical Coater etc. Though the mechanical forces imparted to the coating color dynamics are different in each case, the objectives of the process to control coat weight are the same. Hence, requirements of specific property depend on solid content, speed of the coater, basis weight of pigment-coated paper etc. Generally, the mill routine control parameters are: solid content; pH and low shear viscosity i. e. Brookfield or Fordcup., high shear stability applicable for high solid, high speed systems, water retention, ash and foam content. Out of the so many parameters affecting the coated paper quality or coating performance, the most important is flow characteristics of the coating color. This property affects in various stages of operation starting from pigment make down, storage of pigment, supply and delivery of the slurry for blending with the binder and entire hydrodynamics of the process under action of blade, roll, rod of the coater etc.. Abnormal thickening may also result during blending of pigment and binder. The important parameter for coater performance is coat weight. The coat weight for an inverted trailing blade coater (with either stiff blade or bent blade) is proportional to the square root of viscosity. In connection to coating color rheology, it is important to define the realistic interpretation of the term "rheology" of pigment coating suspension. It appears that the viscosity term is not appropriate in connection with the coating color processing and hence the Rheological behavior needs to be properly evaluated. It has been seen that the coating color dynamics or its flow characteristics, its storage, handling, screening and processing are highly dependent on its rheological behaviour. It is also evident that no unique models can be applied to estimate the rheological characteristics of coating color. It is a fact that it may conform to non-Newtonian pseudoplastic / dilatants or to this along with time dependent property like thixotropy, anti-thixotropy or rheopexy. Thixotropic index and the leveling index (thixotropic index/ app. viscosity at the maximum shear rate) are equally important for evaluation of coating color characteristics. The conditions of transition from one behavior to another behavior are found to have significant influence on mechanics of coating process. The system geometry and configuration have also impact on the overall dynamics of the system. Hydrodynamics force imparted to the system must correspond with the mechanical force.

The nature of coating suspension has to be evaluated by a proper instrument to predict its correct behavior. Selection of the appropriate instrument is thus very much necessary to find the exact nature of fluid. Apart from Brooke Field and Ford Cup, other viscometers like Ferranti Shirley Cone Plate, Hagen Cone Plate Rheometer, Hercules Hi Shear Viscometer, Band viscometer etc. are employed.
This deliberation will include the rheology of pigment dispersion alone or in combination (clay and $CaCO_3$ etc.), rheology of binders and the overall rheology of coating color. How to change or stabilize flow properties of coating color during make-up, storage, handling, and application by increasing or decreasing the shear resistance with various equipments are also very essential. As an example, with air-knife coaters, there is often a need for lowering the viscosity of the color, while other systems may need a different rheology and higher viscosity. Prolonging the storage life (thinning) and lowering of viscosity are

needed for a coating color consisting of binder of the order of 20% , like starch, casein and protein etc. to make them operable by addition of urea and dicyndiamide. On the other hand for higher solid content coating with higher viscosity attainment requires the modification of its rheology by adding small quantities of starch, casein, protein, alginates, carboxymethyl cellulose and many other materials. The state of the art of the coating process in terms of coating Rheology and its impact on coater performance is reviewed in this paper.

LATEXES AS COATING BINDERS



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LATEXES AS COATING BINDERS

Dr. S.V. Govindaraju

Extended Abstract

The journey of the paper and paperboard making from pulping to printing, passes through the penultimate stage of coating. Coating technology has witnessed a continual improvement, both in terms of quality and cost, so as to meet the changing demands of printing technology. Paper (and paperboard) is coated in order to improve its appearance and to impart a smooth and receptive surface for printing. Usual coating ingredients are pigments, latex, water-soluble co-binders, dispersant, alkali, lubricants, insolubilizers, optical brightening agents etc. although the quantity of latex is minor compared to pigment, it is of paramount importance for the satisfactory performance of coating solution during processing and finally during printing. Latex contributes not only to the mechanical stability, rheological and water holding characteristics of coating solution, but also imparts to the coating many properties such as opacity, surface strength, water resistance, ink absorption etc. these properties are indispensable conditions for good printability and appearance of the final properties.

The role of binder in coating process is to bond pigment particles to one another and to the surface of base stock. Though formerly natural binders , such as starch, casein were used, the changing demands of printing technology has given impetus to the invention of synthetic binders. Even synthetic binders have undergone a dramatic change over a period resulting in new generation binders. These new generation binders, which are produced by state-of-the art emulsion technology, improve water holding characteristics, shear stability and high solid rheology.

Latex parameters, such as polymer composition, functional monomer level, glass transition temperature, particle size, molecular structure of the polymer are very important while designing a binder for property balance of printing process. Latex plays a significant role in the coated paper and board properties, such as brightness, opacity sheet gloss, ink absorption (K&N), dry pick resistance, wet pick resistance, print gloss mottle, blister resistance, stiffness etc.

The main purpose of this presentation is to give necessary and sufficient insight on the XSB latex parameters affecting the properties of coated paper and board.

TRG PROGRAMME ON SIZING & COATING, AUG 22-24, 2005

LITERATURE

CENTRAL PULP & PAPER RESEARCH INSTITUTE

PEER-REVIEWED **SURFACE SIZING**

Surface sizing with cationic starch: its effect on paper quality and papermaking process

HAK LAE LEE, JAE YOUNG SHIN, CHANG-HEON KOH, HOON RYU, DONG-JU LEE, AND CHANGMAN SOHN

ABSTRACT: The characteristics of starches used in surface sizing affect not only paper properties but also the efficiency of broke recycling processes. Oxidized starches commonly used for surface sizing tend to penetrate deeply into the paper structure, and this causes substantial reduction of opacity. Furthermore, oxidized starches act as anionic trash in the broke recycling process. To solve the problems associated with conventional size press starches, cationic starches were prepared and their effects on paper properties and papermaking processes were investigated. Results showed that cationic starches outperformed oxidized starches in opacity, brightness, print gloss, and ink density due to their better holdout property. Effectiveness in surface holdout of cationic starches was verified using a confocal laser scanning microscope (CLSM). Adsorption ratio of the cationic starch onto fiber was substantially larger than that of oxidized starch, and this decreased COD load and increased fines retention and strength. We observed improvements in stiffness, opacity, brightness, printing quality, and picking resistance when ammonium persulfate starch was substituted with cationic starch in the film transfer size press. Furthermore, diverse beneficial effects of improving white water quality, including the reduction of COD and cationic demand, were obtained. Surface sizing with cationic starch also gave better picking resistance and ink receptivity for coated paper than ammonium persulfate starch.

Application: To solve problems associated with oxidized starches, we prepared cationic starches and investigated their effects on paper properties and papermaking processes in laboratory and mill settings.

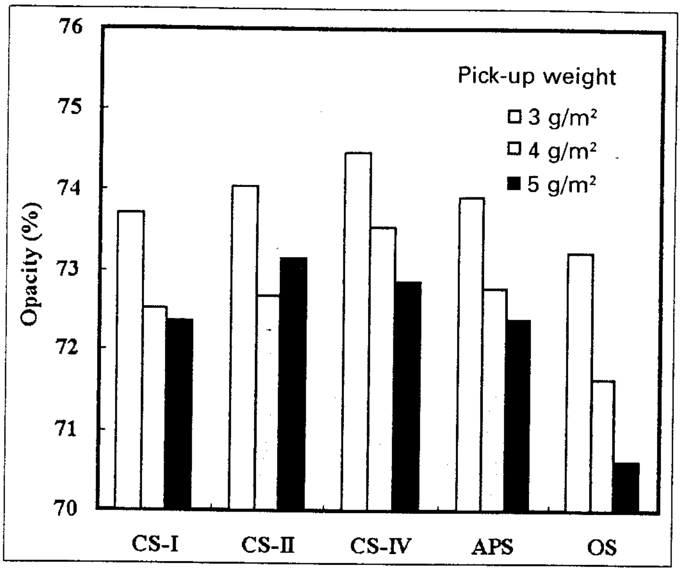
Traditionally, the paper industry consumes a large quantity of starches as internal and external additives. The purpose of external application of starch solution onto dried paper or surface sizing is to provide resistance to penetration of liquids, to give better surface properties, and to improve certain physical properties of paper sheet such as tensile strength and internal bond. To achieve this purpose effectively on today's high-speed paper machines, many technological developments have been made in surface sizing equipment during the last several decades. Klass [1] provides an excellent review on the development of size press technology. Among the new technologies, metering size presses provide solutions to some of the problems associated with the conventional size press, including improved surface starch application, increase of machine speed and runnability, etc.

Although surface sizing provides many advantages in improving paper properties without contaminating the wet end, a substantial proportion of the size press starches re-enter the papermaking system through the broke recycling process. It is quite common for more than 10% of the total production to become broke. If this contains 5% of surface sizing agents, more than 0.5% of the total furnish will consist of size press starch, which is introduced into the papermaking system along with the broke. Therefore, for a paper mill producing 1000 ton/day, 5 tons of size press starches are introduced into its papermaking system every day along with the dry broke. If the size press starch dissolves into white water while reslushing dry broke, severe contamination of process water and effluent will result, and this will limit the level of papermaking system closure.

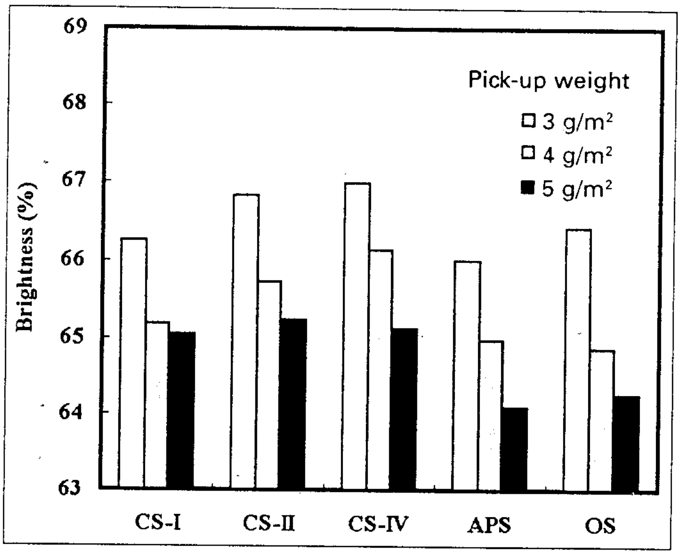
Starches for surface sizing range from the native in-mill converted products to preconverted starches. In-mill converted starches include enzyme-converted starch and ammonium persulfate (AP) converted starch. Oxidized starch, starch ethers and esters, and cationic starches (CS) are examples of preconverted ones, which have been characterized in other studies [2, 3]. If the level and type of size press starch used is inappropriate, it can result in loss of opacity and brightness, lower bulk, reduced machine speed, higher effluent losses, increased sludge build-up, and poor paper machine runnability [4].

During the past decade, many starch manufacturers have introduced cationic size press starches, mainly as an opportunity to reduce the starch load in white water and effluent [4-7]. This environmental benefit of cationic size press starches occurs because the starches remain tightly bound to the fiber even during the repulping of broke, thus preventing the starches being lost in effluent. Studies have shown that cationic starch use nearly halved the BOD level or effluent load [5, 7]. Improvement of paper properties, including ink-jet printability, sizing degree and sheet porosity, could be obtained by using cationic size press starch [6, 7].

The theory behind cationic size press starches is that they will bond with the anionic fiber in the manner of a wet end starch, which means they will form a stronger, more surface-oriented film. The effect is to raise the proportion of starch concentration at the surface to a level higher than is possible with conventional size press starches [4]. Kogler et al. used the concept of using interpolymeric interaction between cationic materials applied on the anionic charged paper surface to promote quick immobilization of coating colors [8]. Fast immobilization of cationic coating colors on anionic paper surface improves fiber coverage and printability. On the other hand, Remmer



1. Effects of starches on opacity. Base sheet opacity was 77.3%.



2. Effects of starches on brightness. Base sheet brightness was 69.6%.

and Eklund [9] showed that the degree of cationization of size press starches had no effect on absorption rate, which was unexpected since cationic starches were assumed to have a higher affinity for the paper fibers than the anionic starch and would therefore be expected to yield a lower absorption rate. In this study, however, Remmer and Eklund [9] defined the absorption rate as the total starch pickup that included starches that remained on the paper surface as well as those that penetrated into paper structure.

In most of the prior studies on cationic size press starches, simple comparisons were made on the effect of a cationic size press starch and other conventional starches on effluent contamination, paper properties, wet end chemistry, etc. [4-7]. In this study, we investigate the effect of four cationic size press starches with different degrees of substitution (DS) and viscosity on paper properties, wet end chemistry, and white water contamination, and compared the results with those of conventional ammonium persulfate and oxidized starches. Since a great amount of papers surface sized on the size press are used as coating base stock, we also examined the influence of size press starch types on the properties of coated papers. Finally, we evaluated the performance of a cationic size press starch on a high-speed paper machine equipped with a film transfer size press.

	CATIONIC STARCH				AMMONIUM PERSULFATE STARCH	OXIDIZED STARCH
	CS-I	CS-II	CS-III	CS-IV		
Brookfield viscosity (cPs)	11	26	11	21	9	9
DS	0.01	0.01	0.03	0.01	-	-

I. Characteristics of starches

EXPERIMENTAL

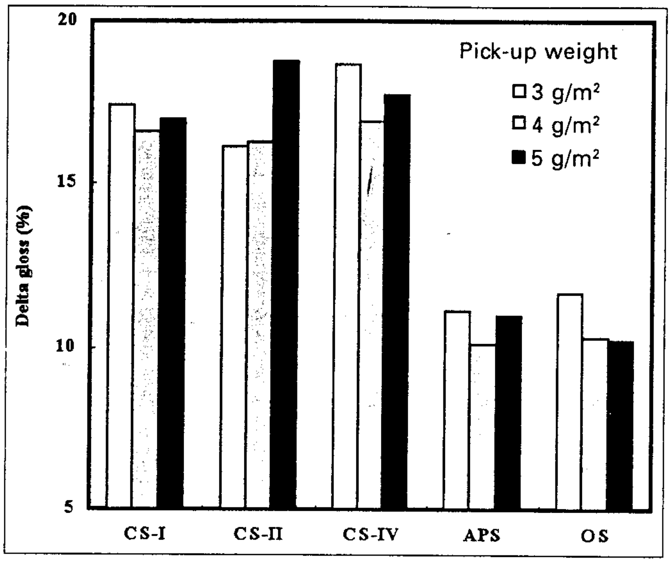
Starches

This study used four cationic starches with different DS and viscosity, ammonium persulfate starch, and oxidized starch, as shown in **Table I**. Ammonium persulfate starch was prepared by reacting 0.45% of ammonium persulfate with starch slurry at 10% consistency. Oxidized starch was prepared with the use of 3% sodium hypochlorite. Brookfield viscosity in Table 1 was measured using 10% starch paste at 50°C. As shown in Table 1, the Brookfield viscosity of ammonium persulfate and oxidized starches were 9 cPs. The viscosity of two cationic starches, CS-I and CS-III, were 11 cPs, while those of CS-II and CS-IV were 26 cPs and 21 cPs, respectively.

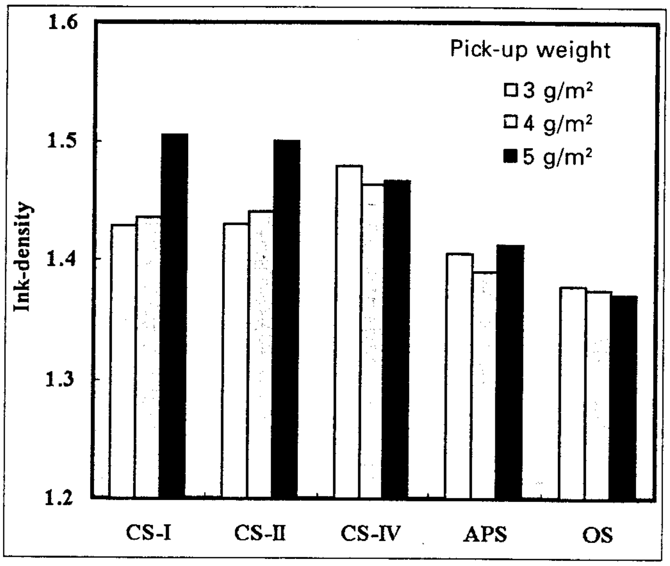
Surface sizing and property measurement

We prepared a starch slurry at 10% concentration and cooked it at a temperature of 95°C for 30 minutes. We kept the cooked starch paste in a constant temperature water bath at 65°C and used it for surface sizing. Coating base stock at a basis weight of 61 g/m² produced on a high speed gap former was used as substrate for the surface sizing experiment. The furnish of this base stock consisted of 80% hardwood bleached kraft pulp and 20% softwood kraft pulp. While producing the unsized base paper the starch solutions on the film transfer size press was substituted with water. The thickness of paper was 75 μm and contained 8% ash. Gurly permeability of the paper was 6.3 ± 0.3 sec. After surface sizing with starch solutions using an automatic rod coater, it was cylinder dried and lightly calendered on a soft calender. Starch pick up ranged from 3-5 g/m². Optical and strength properties of surface sized papers were determined according to TAPPI standards test methods. Delta gloss, trapping and ink density were measured after printing sample strips with cyan ink on RI printability tester. Picking resistance was determined after printing magenta ink with tack value of 18 on RI printability tester.

To investigate the penetration of starch solution into papers, we used confocal laser scanning microscope (CLSM) images for the cross section of the hand-



3. ***Effects of starches on delta gloss. Delta gloss measured on base sheet was 7.2%.***



4. ***Effects of starches on ink density. Ink density on base sheet was 1.29.***

sheets made from 70% bleached hardwood kraft pulp and 30% bleached softwood kraft pulp were obtained after surface sizing with starch solutions containing 0.1% of a fluorescence dye, Aridine-orange C.I. 46005.

Broke recycling

We examined the effect of starch types on broke recycling using surface sized handsheets. The starch dry pickup of these handsheets was 4±0.1 g/m^2. The disintegrated handsheets were mixed with stock consisting of 70% hardwood bleached kraft pulp and 30% softwood kraft pulp, both of which were beaten to 450 mL CSF.The ratio of the recycled surface-sized paper was 30%. We stirred the mixed stock for 60 min at 60°C in the laboratory pulper to extract starches.

Retention measurement and analysis of the filtrate

To evaluate the filler retention in the laboratory, we added 15%-25% of ground calcium carbonate (GCC) to the stock, and used 0.03% of a cationic PAM as a retention aid. The furnish pH was 7.5±0.2. We used a dynamic drainage jar (DDJ) to measure retention according to TAPPI Standard T261cm-90. Cationic demand and COD of DDJ filtrate were measured. Cationic demand was determined with PCD-03, and we used a COD reactor and DR-2000 spectrometer to measure COD. Adsorption of starch onto pulp fiber was evaluated by UV-Visible spectroscopy method. We made handsheets at a basis weight of 75 g/m^2 on a square handsheet former to examine the paper properties. Handsheets consisted of 30% surface-sized broke mixed with bleached kraft pulps, and 20% of GCC and 0.03% of PAM.

Coating

After dispersing No. 1 high brightness, ultrafine clay, 6 pph of starch and 10 pph of S/B latex were added as binders, and coating solids content was adjusted to 50%. We spread the coating onto plastic films to form, then determined the porosity by measuring the weight increase after saturating the coating with silicone oil. We determined brightness and opacity of the coatings by conventional methods.

RESULTS AND DISCUSSION

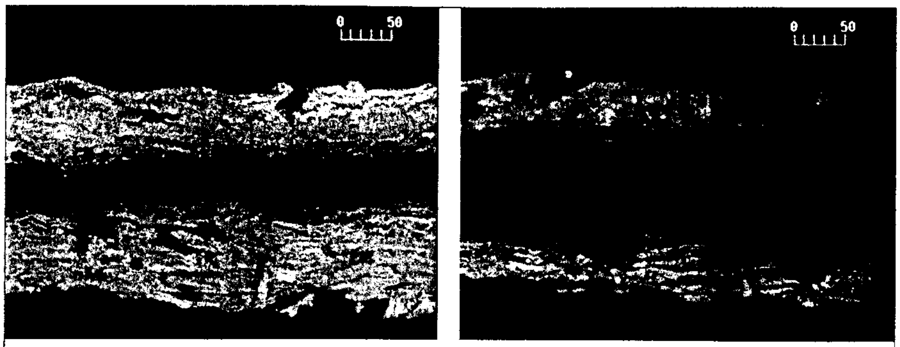
Effect of starch types on paper properties

To investigate the effect of the types of size press starches and the amount of their pickup on paper properties, opacity, brightness, gloss, and ink density were determined after surface sizing unsized base paper with cationic, oxidized and ammonium persulfate starches. The opacity of base sheet was 77.3%. As shown in **Fig. 1**, opacity decreased overall as starch pickup increased. Surface sizing with cationic starches caused less loss in opacity than surface sizing with oxidized starch. CS-IV, which was prepared by adding 3% of waxy maize starch, gave the least reduction in opacity. The high viscosity of CS-IV appeared to be a factor in that. However, CS-II, with a higher viscosity than CS-IV, causes greater reduction in opacity, suggesting that viscosity is not the sole factor for opacity reduction.

Surface sizing also decreased brightness, and brightness reduction increased as the amount of starch pickup increased (**Fig. 2**). The brightness of unsized sheet was 69.6%. Sheets surface sized with cationic starches showed relatively high brightness compared to the sheets surface sized with ammonium persulfate starch because ammonium persulfate starch is yellowish in color. Figures 1 and 2 reveal that the most significant loss of opacity and brightness occurred with oxidized starch. Surface sizing with cationic starches also gave greater delta gloss and ink density than other starches, as shown in **Fig. 3 and Fig. 4**.

These results suggest that cationic starch penetrates less into paper after surface sizing. We used CLSM images of surface-sized handsheets to demonstrate the difference in penetration depth into paper for oxidized and cationic size press starches. CLSM images clearly showed that less penetration into paper occurred when cationic starch (CS-III) was used for surface sizing, i.e. more starch remained on the paper surface (**Fig. 5**). Cationic starches tend to stay on the paper surface rather than penetrating into the paper structure because of the electrostatic interaction between negatively charged fibers and positively charged starch molecules [4]. Oxidized starches tend to penetrate into paper. In other words, when cationic starch is used in surface sizing more internal pore structure of the paper can be preserved. This causes less reduction in opacity and brightness after surface sizing. It also improves printing gloss and ink density.

One of the main objectives of surface sizing with starches is to improve the strength property of papers. Depending upon the penetration depth of size press starch, different effects on paper property will result. This difference in penetration tendency of starches gave differing improvement of tensile strength and stiffness. As shown in **Table II**, handsheets surface sized with oxidized starch showed greater tensile strength, while those surface sized with cationic starch gave better stiffness.



Oxidized starch

Cationic starch

5. CLSM images of the cross section of paper surface sized with oxidized starch (left) or cationic starch (right).

	CATIONIC STARCH-I	AMMONIUM PERSULFATE STARCH	OXIDIZED STARCH
Tensile index (Nm/g)	49.9 ± 0.7	51.5 ± 1.0	51.8 ± 1.1
Stiffness (mNm)	0.503 ± 0.025	0.443 ± 0.027	0.411 ± 0.022

II. Effect of surface sizing starches on tensile strength and stiffness (with test results reported as mean values for 12 measurements along with 95% confidence intervals)

Effect of starch type on broke recycling

Self-retention of size press starch onto fiber surface is critical for reducing white water contamination of the papermaking process and decreasing the loss of raw materials to drain. The amount of starch desorbed when size-pressed paper was recycled was determined using surface sized handsheets. Results showed that around 80% of cationic starch remained adsorbed on the papermaking fiber while 35% of oxidized starch retained adsorbed after repulping. It has been shown that the adsorption of cationic starch onto cellulosic fibers and coating clay is to a great extent governed by the electrostatic interaction between the charged fiber material and cationic starch molecules [10-12]. This high affinity of cationic starches for the cellulosic fibers causes a low BOD load in the effluent water.

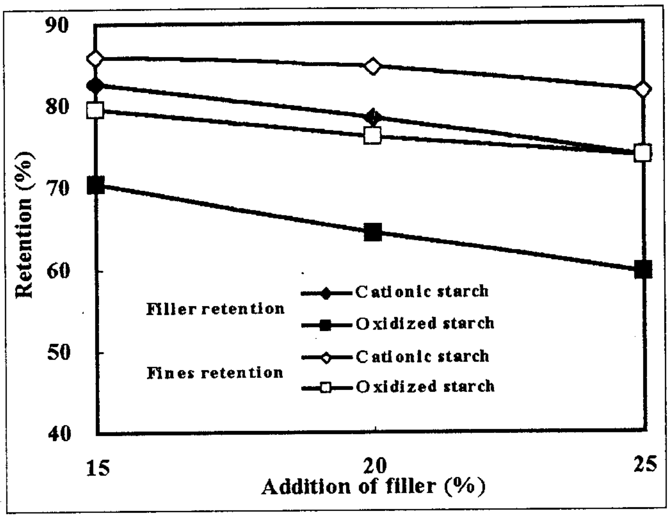
Filler retention decreased around 15% when surface-sized paper with oxidized starch was recycled because anionic starch decreased retention efficiency of the cationic PAM (**Fig. 6**). Similar results were obtained for fines retention indicating that when cationic starch was used for surface sizing less amount of retention aid will be needed for retention. Substitution of oxidized starch with cationic starch for surface sizing reduced the cationic demand of white water filtrate more than 25%. COD of white water also decreased more than 50 ppm when cationic size press starch was used (**Fig. 7**).

The detrimental impact of oxidized starch desorbed from the recycled papers increases exponentially as the white water closure increases [13]. Furthermore, the temperature of the papermaking system increases with the increase of the closure level and this enhances the ratio of starch desorption from the broke [6]. Thus, the advantages of using cationic starches increases when the level of papermaking system closure is increased.

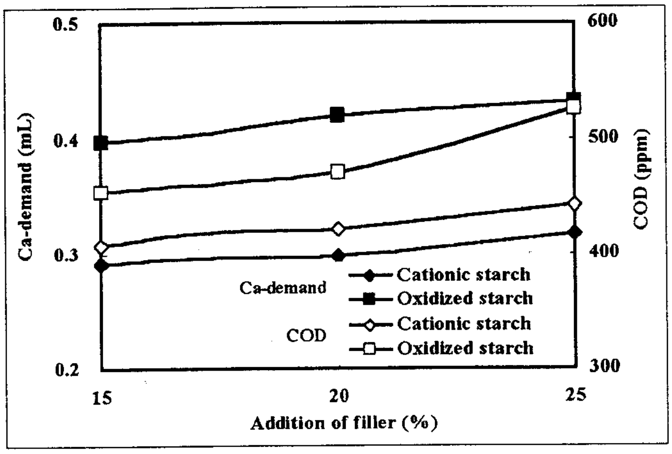
Effect of starch types on pigment coating

The interaction between coating color component and base stock is critical for the structural formation of coating layers. The concept of improving fiber coverage using a cationic coating color that rapidly immobilizes through interpolymeric complex formation with the anionic paper surface has been exploited. Other studies obtained better coverage and improvement of optical and printing properties at a lower blade pressure and coat weight [8]. Implementation of this concept is still delayed, however, because expensive coating ingredients are required. Research suggests that electrostatic interactions between the paper substrate and coating color which promote destabilization or flocculation would promote rapid immobilization and increase the porosity and many properties associated with the pore structure of the coating including opacity, brightness, ink absorption, etc [14, 15]. It is quite logical, therefore, to expect to have more structured coating with greater pore volume when cationic starch was used for surface sizing the base stock because there will be stronger electrostatic interaction between the cationic paper surface and anionic coating components.

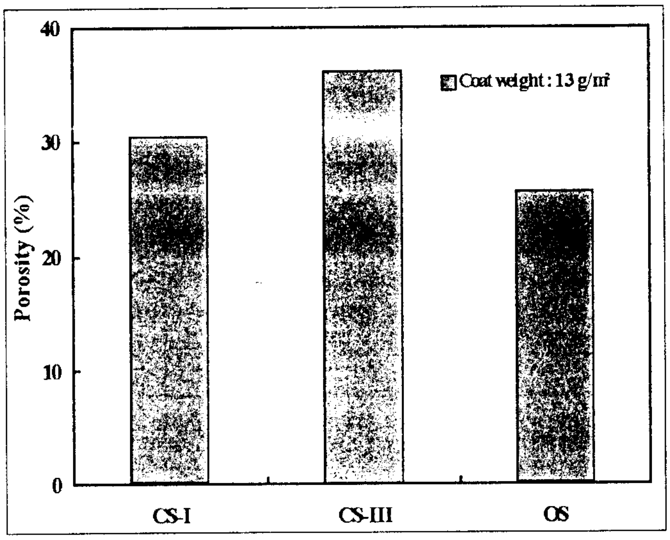
To investigate this hypothesis, we coated transparent plastic films with either cationic starch or oxidized starch. We applied pigment coating onto these films to reach 13 g/m^2 of coat weight. Our results showed that the coating layer formed on the substrate surface sized with a cationic starch (CS-III) gave the highest pore volume. The coating formed on the substrate surface sized with oxidized starch showed the lowest pore volume (**Fig. 8**). Higher brightness



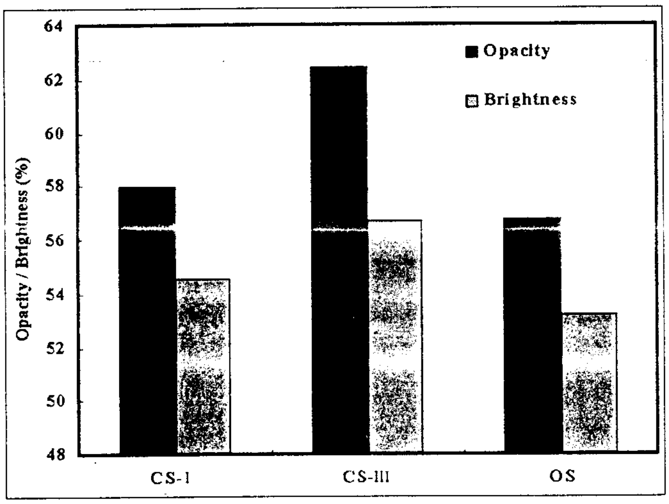
6. Filler and fines retention vs. filler addition for cationic and oxidized starches.



7. Cationic demand and COD of the DDJ filtrates.



8. Effects of starches on coating porosity.



9. Effect of starches on opacity and brightness of coating formed on plastic film.

and opacity also were obtained for the coatings formed on the plastic film surface sized with CS-III (**Fig. 9**). The fact that CS-III-with a higher degree of substitution-gave the highest porosity indicates that stronger interaction is beneficial for creating more pore volume in the coating.

Mill experiences

We tested the benefits of using cationic starch at the size press on PM 23 (which was equipped with a film transfer size press) of Hansol Paper Company for 34 days from August 31 to October 3, 2000. This machine produces coating base stock in alkaline condition. Its average machine speed during the trial period was about 1150 m/min. The average furnish composition during this trial was 75% hardwood bleached kraft pulp and 25% other pulps consisting of softwood bleached kraft pulp and BCTMP. The degree of substitution of the cationic starch was 0.015, and the viscosity of 10% starch solution ranged from 10-15 cPs.

Properties of surface-sized paper before and after pigment coating were determined, and the average of 10 measurements was reported. Paper properties evaluated were ash content, starch pickup, internal bond strength, stiffness, and gloss. Ash content was determined after ashing the paper at 525°C. Picking resistance, trapping and ink setting were determined with RI printability tester. Same inks and methods as used to carry out the RI printability tests for the laboratory prepared sheets were employed. Starch content, COD and conductivity for the stock samples taken from the headbox and silo were monitored. Enzymatic test method was used to determine the starch content [16].

Table III shows representative results obtained from the mill trial. As seen here coating base papers with better internal bond strength and picking resistance were obtained when ammonium persulfate starch was substituted with cationic starch at the size press. When these papers were coated, improvement in ink set and trapping were obtained; gloss and picking resistance were about the same. This was very promising since the paper size pressed with cationic starch contained more ash and had slightly less amount of size press starch than the paper sized pressed with ammonium persulfate starch.

When the ash contents of papers were maintained more or less constant, even greater improvement in internal bond strength, stiffness, and picking resistance of base paper were obtained when we used cationic size press starch. In addition, substantial increases in print gloss, stiffness and picking resistance for coated papers were achieved when cationic starch was used, as shown in **Table IV**. This suggests that cost reductions are possible by using more fillers when cationic size press starch is used. It was surprising to see that cationic size press starch improved internal bond strength of base paper. Oxidized size press starch tends to penetrate deeply into paper structure, while cationic starch tends to stay on the surface (Fig. 5). The results obtained from laboratory handsheets showed that oxidized starch gave better internal bond strength as well [17]. We attributed the greater internal bond strength obtained when cationic starch was used at the size press to the greater amount of cationic starch left on fiber surface after repulping due to its lower extractable character. That allowed the starch remaining on fiber surfaces to act as dry strength agents.

Improvement of strength properties achieved using cationic starch at the size press allows for an increase in filler content and resulting cost reductions [6]. Consequently, we examined the possibility of increasing filler levels. During this mill trial the ash content of the coating base paper at a basis weight of 63 g/m^2 increased from 15.4%-16.6% to 16.9%-18.9%. The results indicated that internal bond strength increased more than 30%, and stiffness and picking resistance remained rather constant although the ash content increased as mush as 2.0% (**Table V**).

To examine the desorbing tendency of size press starches into white water, we determined the starch contents in the headbox and silo. As shown in **Table VI**, substitution of ammonium persulfate starch with cationic starch resulted in the

PROPERTY	AMMONIUM PERSULFATE STARCH	CATIONIC STARCH
Base paper property		
Surface sizing starch (%)	5.15	5.03
Ash content (%)	14.53	15.50
Scott internal bond strength (ft·lb×10^{-3})	165	250
RI picking resistance	4.1/4.3	4.3/4.5
Coated paper property		
Paper gloss (%)	72.0	72.5
Printing gloss (%)	78.3	78.5
RI picking resistance	4.0/4.3	4.1/4.3
Ink set	4.1/3.8	4.5/4.3
Trapping	4.0/3.8	4.3/4.2

III. Properties of coating base stock (74 g/m^2) and coated paper (104 g/m^2)

PROPERTY	AMMONIUM PERSULFATE STARCH	CATIONIC STARCH
Base paper property		
Surface sizing starch (%)	4.73	5.03
Ash content (%)	15.41	15.50
Scott internal bond strength (ft·lb×10^{-3})	170	250
Stiffness (mNm)	72.0	74.5
RI picking resistance	3.8/4.0	4.3/4.5
Coated paper property		
Paper gloss (%)	40.5	41.5
Printing gloss (%)	67.8	70.5
Stiffness	63.0	71.8
RI picking resistance	3.9/4.2	4.3/4.3
Trapping	4.0/4.2	4.0/4.2

IV. Properties of coating base stock (63 g/m^2) and coated paper (80 g/m^2)

	AMMONIUM PERSULFATE STARCH		CATIONIC STARCH				
Ash content (%)	15.4	16.6	18.8	18.9	16.9	17.4	17.7
Internal bond (ft·lb×10^{-3})	170	175	240	235	260	240	250
Stiffness (mNm)	72.0	67.3	68.5	66.0	70.3	68.8	67.0
Picking resistance	4.0	3.9	4.2	-	4.1	-	4.0

V. Comparative study for increasing ash content of a coating base paper

	AMMONIUM PERSULFATE STARCH	CATIONIC STARCH	REDUCTION (%)
Starch content (ppm)			
Headbox	680	280	59
Silo	650	250	62
COD (ppm)			
Headbox	1400	1000	29
Silo	1380	980	29
Conductivity (mS/cm)			
Headbox	1.4	1.2	14
Silo	1.4	1.2	14

VI. Wet end analysis results

reduction of starch content by about 60%, indicating that substantially greater amounts of cationic size press starches remained on fiber surfaces during broke recycling. This would be very effective in reducing anionic trash in the process water and in utilizing raw materials more effectively. COD and conductivity in the headbox and silo decreased when we used cationic starch. Reductions in COD will result in effluent load reductions, and lower conductivity will improve the effectiveness of many polyelectrolytes.

We also measured ash content at the storage tank of the size press during the mill trial. We found that average ash content of the size press starch decreased from 2.16% to 1.52% after substituting ammonium persulfate starch with cationic starch. The ash contents of cationic starch and ammonium persulfate starch were 0.8% and 0.1%, respectively. This indicates that the reduction of ash content in the size press starch is not due to starches used. Since the ash in the starch tank derives from the fillers detached from the paper surface, this level is closely related to the runnability of the film transfer size press equipped with rod bars.

CONCLUSIONS

Use of oxidized starches at the size press causes diverse problems in broke recycling and reduces opacity, brightness and printing properties because of their anionic character. To solve these problems associated with oxidized starches cationic starches were prepared and the effects of the type of cationic starches on paper properties and papermaking processes were investigated.

Results showed that cationic starches have pronounced effects in improving opacity, brightness, print gloss, and ink density of paper due to its better holdout property. Effectiveness in surface holdout of cationic starches was verified by CLSM. Adsorption ratio of the cationic starch onto fiber was 80%, which was substantially larger than that of oxidized starch. This decreased COD load in white water by more than 50 ppm and increased fines retention and strengths of handsheets. Base papers surface sized with cationic starch also gave better opacity and brightness of coated paper.

When cationic starch was used as size press starch for a film transfer size press the starch contents in headbox and white water silo were decreased by 59%-62% and 29%, respectively. Improvement in internal bond strength, stiffness, and picking resistance of paper was obtained when ammonium persulfate starch was substituted with cationic starch and this allowed the room to use more fillers. **TJ**

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Effective Sizing of Waste Paper Containing Calcium Carbonate with Rosin and Alum System

Kapoor S.K., Sood Y.V., Tyagi S., Manoth M., Bharti

ABSTRACT

Paper mills in India use different types of waste paper in the production of various paper grades ranging from cultural to packaging. The waste papers of foreign origin are generally neutral sized containing substantial amount of Calcium carbonate as filler. Recycling of such type of papers give problem in sizing with rosin soap and alum under acidic conditions. The present studies indicated that such paper could be suitably sized by using dispersed fortified rosin at pH 6.2. The pH can be controlled by using either alum or Poly aluminium Chloride (PAC) or by the mixture of both. PAC did not show advantage over alum up to pH 6.2 however it was more effective at higher pH levels. Premixing of dispersed rosin size with alum prior to addition to the stock gave better sizing than separate addition. Addition of cationic starch gave improvement in the sizing with dispersed rosin where as not much effect was observed for rosin soap size. The rosin-alum system may not match the performance of common neutral sizes under all conditions; however, it gives a viable alternative to raise the wet end pH close to neutral level. Plackett Burman statistical evaluation of different process variables on sizing indicated that more effective variables were Sizing dose > Stock temperature > filler amount > cationic starch.

INTRODUCTION

All over the world, the trend of using recycled fibers for papermaking is increasing. Recycled fiber has become an important element in pulp and paper business. The key driving force for the utilization of recycled fibers has traditionally been economics. In India, paper industry is rapidly shifting towards paper making from raw materials other than wood. The agricultural residues and wastepaper have emerged as two main alternatives to the forest based raw materials. Today about 63% of paper mills in India are using waste paper as raw material and it accounts for 31% of total paper production. The supplies of waste paper in India are from eastern countries, Middle East and USA. One of the major problems with the imported papers is that these are

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generally alkaline/neutral sized containing substantial amount of $CaCO_3$ as filler. Recycling of waste paper containing $CaCO_3$ therefore tends to give problems in acid process owing to the decomposition of $CaCO_3$. This decomposition results in accumulation of sparingly soluble gypsum (calcium sulphate) and calcium hardness in the white water, with the liberation of carbon dioxide.

The $CaCO_3$ filled papers when repulped and sized with Rosin soap/alum under acidic pH condition give problems like severe pH swings, excessive alum and size consumption, loss of filler, high deposit problem, foaming, etc in the system. To overcome these problems it is advisable to size such paper at neutral or close to neutral pH. The reactive sizes available are alkyl ketene dimmers (AKD) and alkenyl succinic anhydrides (ASA). However, it is well-known that sizing with synthetic sizes becomes more difficult and uneconomical when the proportion of "trash" and detrimental substances are sufficient in paper pulp [1]. It is generally considered that the concentration of trash material increases with pH. In an acid system, alum act as a remedy to bind or coagulate un wanted components while, in alkaline systems containing $CaCO_3$, pH depression to the "alum level" would not be acceptable. Keeping all these in view the development of close to neutral pH with rosin is being preferred now a days.

In the present investigations different ways of sizing the waste paper containing $CaCO_3$ have been studied with the objective of making properly sized paper. Different process variables like amount of dispersed rosin size, Alum PAC ratio, amount of cationic starch, filler amount, residual hypo, stock temperature and mode of mixing which affect the paper sizing have also been studied using Plackett Burman statistical model.

RESULTS AND DISCUSSION

Sizing with fortified rosin soap size and dispersed fortified rosin size were tried for waste paper containing $CaCO_3$ and without $CaCO_3$. The sizing response of these is shown in Fig. 1 There is a marked difference in sizing response between wastepaper containing no $CaCO_3$ and waste paper containing $CaCO_3$ with rosin soap size/alum at 4.5 pH. At this pH, with Rosin soap size, wastepaper containing no $CaCO_3$ develops a good sizing while waste paper containing $CaCO_3$ shows poor sizing. At the same pH, when sizing was carried out with Dispersed rosin size, sizing response for both types of pulps improved in comparison to Rosin soap sizing and the difference in sizing response between wastepaper containing no $CaCO_3$ and waste paper containing $CaCO_3$ also narrows down. However the decomposition of filler to the extent of 40% was observed at this pH. When pH was increased to 6.2, Dispersed rosin size shows effective sizing with both wastepapers. Also the loss of $CaCO_3$ was relatively lessened (6%) at this pH.

Dispersed rosin showed relatively more improvement in sizing than rosin soap with the increment in size dosage (Fig. 2). Fig. 3 illustrates the effect of stock pH on the degree of sizing on waste paper containing $CaCO_3$, with rosin soap / alum and dispersed rosin / alum systems. At the pH range 4 to 6.2 dispersed rosin acid/ alum system shows effective sizing. However rosin soap/alum system fails to give effective sizing above pH value of 5.0. The effective sizing at 4.2 to 5.0 pH, is probably due to the highest charge density of alum at this pH [2].

MECHANISM OF SIZING

These observations can be explained on the basis of sizing mechanism of Dispersed rosin and Rosin soap. Soap size reacts with alum as soon as it is added to the paper stock. Both electro static bonding and co-ordinate bonding participate in this reaction, which obviously results in a strong bond complex as illustrated in Fig. 4. Since alum is able to form ionic and co-ordinate bonds with rosin only at acidic pH, sizing with soap size has to be developed in the low pH region [2].

On the other hand, dispersed rosin size consists of rosin acid droplets, which have considerable surface areas. Therefore, its retention is a consequence of colloid and surface chemistry. Dispersed rosin does not react readily with alum to form an aluminium resinate. The alum acts as a bridge between the negatively charged fibre and, the negatively charged rosin micelle Fig. 5.

The most significant property of the dispersed size is its reduced reactivity to form rasinate as it enters the paper machine water system. Soap sizes cannot be used in $CaCO_3$ systems as they quickly exchange their sodium ions to form resinate and Ca++ion, which in turn interferes with size. The presence of Ca++ion would compete with alum and form calcium soap which is reported to reduce sizing [3].

Fig. 1 Sizing of waste paper with rosin soap and dispersed rosin at different pH

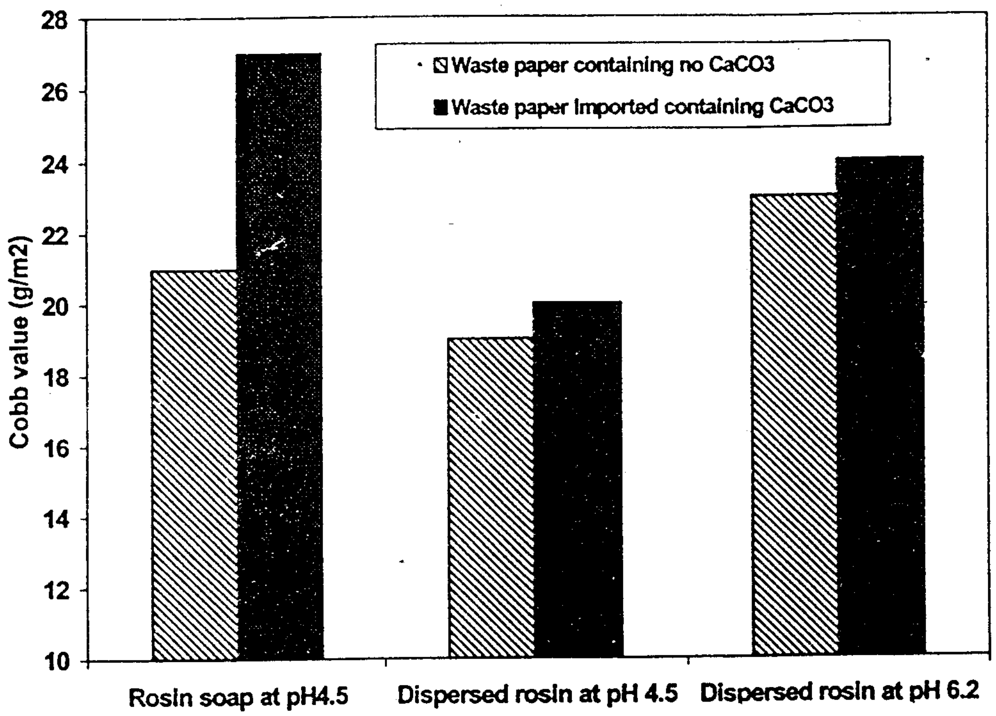
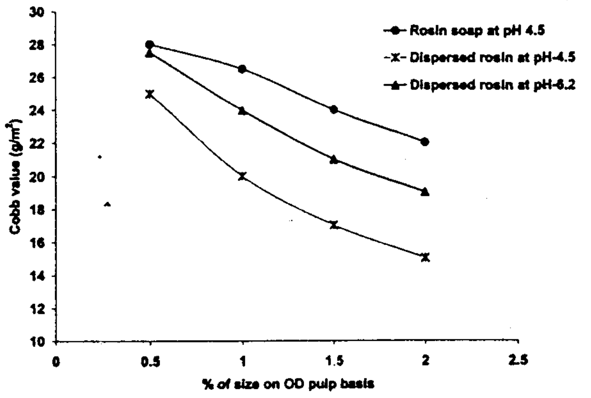


Fig.2 Effect of size dosage on sizing on cobb value at different pH level



Many researchers have described the strong reactivity of alum with cellulosic fibre at higher pH. Alum hydrolyses as pH increases to form colloidal aluminium aggregates [4] which can help to retain the size due to their strong surface activity. As pH increases, aluminium species, have higher adsorption on fibres [5-8], which is no doubt beneficial to sizing.

In a rosin - alum system rosin in either its free acid or soap form will react with alum to give the aluminium ester products which create hydrophobicity. In the case of soap rosin size under acidic conditions, most of the rosin reacts rapidly with alum in solution to give the aluminium ester. In case of dispersed rosin size the reaction of rosin acid and alum does not proceed in solution, but occurs on the fibre surfaces in the drier section. The dispersed rosin size particles are relatively free to migrate during the drying process, throughout the paper web. However, as the paper temperature increases on its movement over the drying cylinders, the heat creates a sintering process where the rosin particles melt and distribute uniformly over the surface area of the fibres to form the aluminium resinate [9]

ADDITION OF PAC

Addition of PAC in place of alum did not show much difference in sizing improvement upto pH value of 6.2. At pH higher than 6.2 PAC showed better effect indicating that addition of PAC will be required at higher pH (Fig. 6). Different modes of

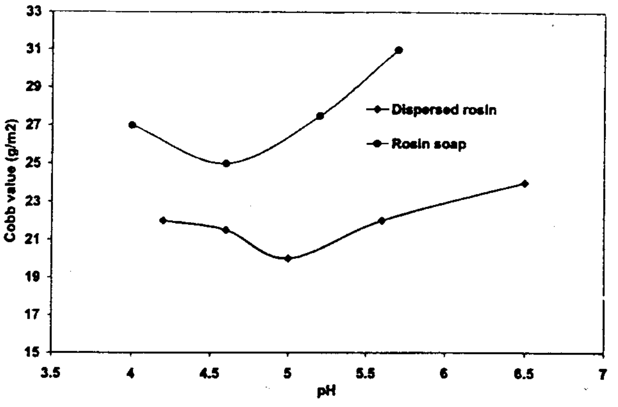


Fig.3 Effect of pH on sizing with rosin soap and dispersed rosin

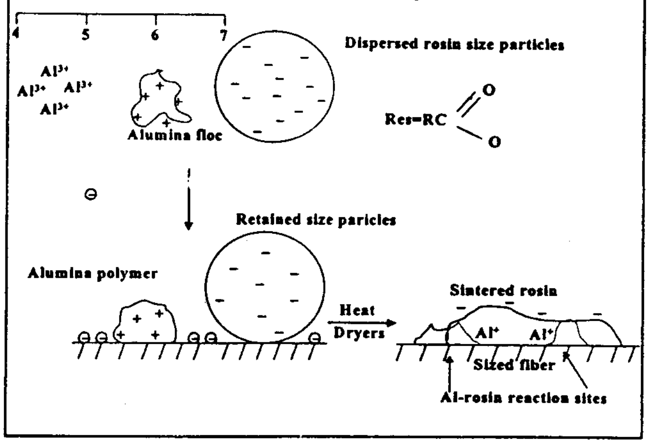


Fig. 5 Mechanism of sizing with dispersed rosin/alum

addition of alum and PAC play an important role on the sizing efficiency especially at neutral pH. Two modes of mixing were tried. One separate i.e. rosin size followed by alum/PAC, another pre-mixing in which alum/PAC was mixed with rosin size and then the mixture of these two was mixed to the thick stock. An improvement in the cobb value of hand sheets was observed when rosin size and alum/PAC were pre-mixed as shown in Fig. 6. Pre-Mixing allows interaction in an environment where the cationic charge of alum/PAC is higher than it would be in the elevated pH stock. Hence, a higher degree of reactivity is achieved with available rosin leading to increased retention and sizing. Premixing of Dispersed rosin and alum/PAC and addition to thick stock allows the formation of the discrete aluminium/size particles immediately in the presence of the fibre.

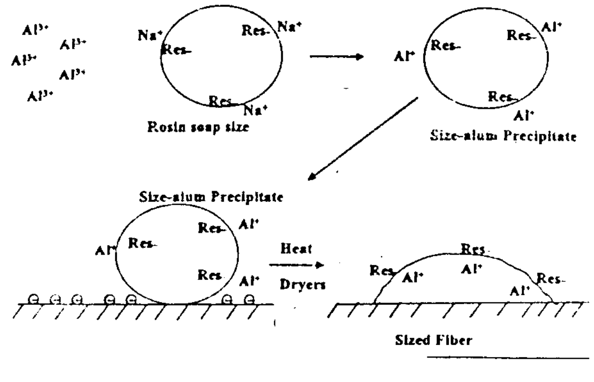


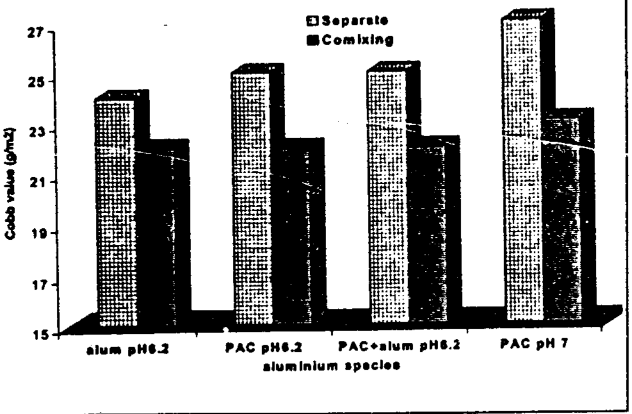
Fig. 4 Mechanism of sizing with rosin soap/alum

This minimizes any opportunity for polyanions or cations to interfere in the case of waste paper containing $CaCO_3$.

ADDITION OF CATIONIC STARCH IN SIZING

The addition of cationic starch in the stock further improves the sizing response in case of dispersed rosin. Since dispersed rosin sizes, are the dispersion of free rosin acids, which have considerable surface areas. Therefore, its retention is a consequence of colloid and surface chemistry and is facilitated by conventional retention aids like cationic starch, which can bridge between surfaces. Cationic starch being a high molecular weight polyelectrolyte, creates electrostatically assisted multiple bond that helps to anchor the dispersed size particle. This also assures good attachment under high shear. Fig. 7 shows the effect of cationic starch on sizing efficiency of two types of rosin sizes. With the addition of 0.5% of cationic starch, the cobb value decreases in case of dispersed rosin size. The decrease in the cobb value is more at 6.2 pH that at 4.5 pH for dispersed rosin size. By adding cationic starch and premixing of alum & dispersed rosin sizing can be improved further. Rosin soap sizes on other hand did not show such improvment in sizing on the addition of cationic starch. This suggests that cationic starch is more suitable for sizing with dispersed rosin sizes for neutral application. An added feature of cationic starch is that it also functions as the retention aid for fines and filler, improving first pass retention.

Fig.6 Effect of mode of addition on cobb value



EFFECT OF DIFFERENT PROCESS VARIABLES ON SIZING

Since paper making stock is the complex mixture of fibers, fiber fines, fillers, sizing chemicals retention aids, slimicides etc. it was decided to check the effect of selected seven process variables on sizing of waste paper. The relative effect of seven process variables on imported waste paper pulp (with $CaCO_3$) has been studied using a Plackett-Burman statistical design.

PLACKETT-BURMAN DESIGN

In this type of experimental design [10], two levels of each variable were selected as given in Table-I.

The high (+) and low (-) levels are chosen far enough apart to expect as significant response in sizing properties, but not so remote from normal stock preparation conditions which are usually practiced in mill. The assumption made was that with in the restricted range of each variable, the response is essentially linear.

Table-II shows the combination of sizing conditions for waste paper pulp containing $CaCO_3$ used in the experimental setup.

The sizing degree of hand sheets, evaluated by Cobb and contact angle are given in Table-III

Fig.7 Effect of addition of cationic starch on cobb value

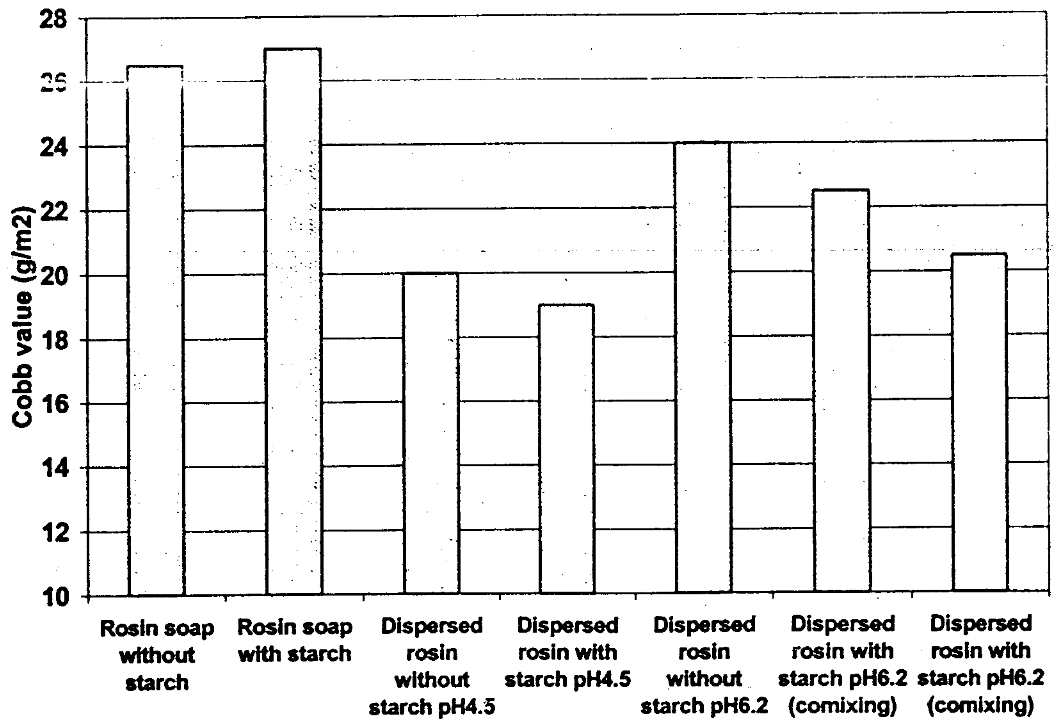


Table-I

S.No.	Process Variables	Process Variable Conditions	
		Low level (-)	High levle (+)
A	Dispersed rosin size (%)	1	2
B	Alum/PAC ratio	1:0	1:1
C	Cationic starch (%)	0.2	1
D	Filler amount (%)	10	30
E	Residual Hypo (%)	0	0.5
F	Stock Temperature (°C)	20	50
G	Mode of Mixing	Seperately mixed	Pre-mixed

Table-II Sizing conditions used in accordance to Plackett - Burman design

Experiment No.	A	B	C	D	E	F	G
1	+	+	+	-	+	-	-
2	-	+	+	+	-	+	-
3	-	-	+	+	+	-	+
4	+	-	-	+	+	+	-
5	-	+	-	-	+	+	+
6	+	-	+	-	-	+	+
7	+	+	-	+	-	-	+
8	-	-	-	-	-	-	-

Table-III Cobb & Contact angle values for different experiments

Experiment No.	1	2	3	4	5	6	7	8
Cobb Value (g/m²)	19	52	42	47.4	48.7	21.4	23.5	41.4
Contact Angle °	109°	53°	72°	68°	61°	101°	96°	76°

The relative ranking as process variable was evaluated and the results were recorded in Table-IV

The results indicated that the variables mainly affecting the cobb value and contact angle of handsheets are the amount of dispersed rosin size, stock temperature and the amount of filler added. The main effect of -18.2 means that when the amount

Table-IV Main effect of Process variables of sizing and their relative ranking

S.No.	Process Variables	Cobb Value	Contact angle
A.	Amount of dispersed rosin size	-18.2 (1)	+27.75 (1)
B.	Alum/PAC ratio	-2.25 (7)	+0.25(7)
C.	Amount of cationic starch	-6.65 (4)	+8.75 (4)
D	Amount of filler	+ 8.6 (3)	-14.75 (3)
E.	Residual Hypo	+ 4.7 (6)	- 3.75 (6)
F.	Stock Temperature	+ 10.9 (2)	-17.25 (2)
G.	Mode of mixing	- 6.05 (5)	+5.75 (5)
* Figures in parenthesis are the rank number.			

Table-V Most Influential Process Variables for Sizing of waste paper

Property	Process variables	Main effect as % of mean
	1. Amount of dispersed rosin size	-49.32%
Cobb value (g/m^2)	2. Stock Temperature	+29.54%
	3. Amount of filler	+23.3%
	4. Cationic starch	-18.02%
	1. Amount of dispersed rosin size	+34.96%
Contact angle (^{0})	2. Stock Temperature	-21.73%
	3. Amount of filler	-18.58%
	4. Cationic starch	+11.02%

of size increased from low level (1%) to high level (2%). there is a decrease in cobb value (as indicated by-ve sign) which implies that sizing improves with addition of dispersed rosin size. This is in accordance to our earlier findings in studying the effect of rosin size dosage on sizing performance. Similarly, the value of 10.9 for process variable-stock temperature indicates that when stock temperature increases from its low level (20°C) to higher level (50°C). the cobb value increases (as indicated by +ve singn). which implies that sizing falls drastically wth the rise in stock temperature. Same is the case with other variables. The relative rank of effectiveness of different process variables remains same when sizing of paper was checked by contact angle method, although the sign got reversed. The sign reversal is due to the fact that increase in contact angle values indicates sizing improvment

RELATIVE EFFECT OF MAJOR PROCESS VARIABLES

Table-V shows the major influential process variables and their effect on sizing property of waste paper. The effect here has been expressed as a percentage of the mean values of cobb values. This immediately demonstrates that when sizing was checked by cobb value, amount of dispersed rosin and stock temperature were particularly sensitive. Similarly amount of filler is more sensitive than amount of cationic starch.

EXPERIMENTAL

The waste paper pulp used for the above experiments was procured from a mill based on waste paper as raw material. The pulp contained 20% $CaCO_3$ filler. The pulp was sized with Rosin soap/Dispersed rosin. The dispersed rosin used was white emulsion, fortified anionic in nature having pH 6. Rosin soap used was fortified, anionic in nature having pH value of 8.5. Handsheets were made on Rapid Kothen sheet former according to the ISO standard method TO6/565N706. The hand sheets were conditioned at temperature 27± 1°C and 65 ±2% relative humidity prior to testing. Cobb value was tested as per standard Tappi Method 441om-90 and contact angle measured as per standard Scan method P18:66

CONCLUSIONS

- Dispersed fortified rosin and alum can be used as a sizing system for making paper from waste paper containing $CaCO_3$. This system has significant advantages over common acid sizing system using rosin soap and alum & is operable over a wide range of pH.
- Sizing of waste paper containing $CaCO_3$ can be done more effectively using dispersed fortified rosin rather than rosin soap.
- Dispersed rosin works effectively at pH range 4.5 to 6.2. At 4.5 pH the decomposition of $CaCO_3$ to the level of 40% was observed where at it was only 6% at pH levels of 6.2
- PAC in place of alum did not show much advantage up to pH level of 6.2, however going to higher pH 7.0 addition of PAC was found to be useful.
- Premixing of dispersed rosin with alum/PAC showed better sizing than normal practice of separate addition.
- Addition of cationic starch produced better effect in sizing dispersed rosin at 6.2 pH than acidic sizing.
- The process variables which affect sizing in descending order were found to be Sizing dose > Stock temperature > filler amount > cationic starch.

ACKNOWLEDGEMENT

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Effect of Acidic and Neutral Sizing on the Strength and Printability of Indigenous Pulps

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ABSTRACT

Sizing of pulp blends of mixed hardwoods and bamboo, mixed agricultural residues and jute the common furnish components of Indian large and medium sized mills were studied using fortified rosin soap under acidic condition, ASA emulsion and dispersed rosin under neutral conditions. It was observed that better sizing is obtained on sizing with 0.6 % ASA emulsion than 0.8 % dispersed rosin at neutral pH and 0.8 % fortified rosin soap at acidic pH. The extent of sizing development in case of agricultural residue pulps is lower than hardwood pulps at the same dosage level of sizing chemical. Addition of talc helps in improving the sizing for both pulp blends. ASA emulsion gave paper of better bonding characteristics than rosin sizes. The print quality as assessed by print density was however observed to be best for dispersed rosin sized paper. The optical properties reversion is more for acidic sized sheets than ASA and dispersed rosin sized at neutral pH.

INTRODUCTION

Indian paper industry has gone through a phase of chemical evolution in last two decades. Different new formulations of process and product additives have been introduced in the market and the sizing chemicals are one of them (1-11). From the conventional acid system with rosin paste and fortified rosin soap to neutral rosin dispersions, the industry is slowly changing to neutral/alkaline system with synthetic sizing materials like ASA (Alkenyl succinic anhydride) & AKD (Alkyl ketene dimer). The driving forces for the change are process advantage, product improvement and environmental considerations. The main advantages of neutral/ alkaline system over acid system are-

- Improved sheet strength.
- Improved paper stability on aging.
- Increased machine runnability, hence increased productivity
- Reduction in energy consumption.
- Increased use of $CaCO^3$ filled recycled fibres.
- Reduction in corrosion.
- Increased system closure.

Besides these advantages, there are few problems inherited with the neutral/ alkaline papermaking like low frictional coefficient of AKD sized paper, unstable sizing or difficulty in controlling sizing level, instability of size emulsion and their handling problems and formations of deposits in the papermaking system. In such scenario, sizing at nearly neutral pH with dispersed rosin emulsion offers good alternative with improved paper strength properties and machine runnability. The primary difference between rosin and reactive sizes AKD, ASA is that in rosin sizing it is rosin and aluminum species that are ionically bonded to each other and these precipitates render the fibers hydrophobic.

In the case of reactive sizes, a covalent bond is formed between the hydrophobic molecule and cellulose of the pulp fibers. A further difference is with the chemical structure of hydrophobic part. In case of rosin it is in the form of fused ring arrangement of aromatic ring whereas with reactive sizes it is typically a long hydrocarbon chain of aliphatic origin. The development of alkenyl succinic anhydride as sizing agent came later than the alkyl ketene dimer and took place in 1974 (5). Like AKD's they are also able to undergo reaction with cellulose and water. The ASA's are considerably more reactive than AKD's and can promote sizing without heat treatment (6). Unlike the AKD's which are derived from fatty acids, the ASA's are petrochemical based. ASA is an unsaturated fatty acid anhydride and is the most reactive amongst sizing agents. It must be emulsified on site and must be used shortly after

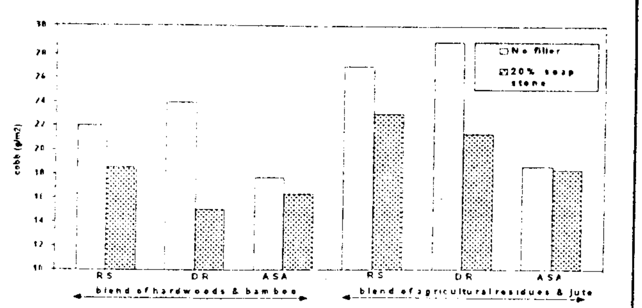

Fig. 1 Sizing response of different sizing chemicals on blends of mixed hardwoods & bamboo, agricultural residues & Jute pulp
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhdride at pH > 7

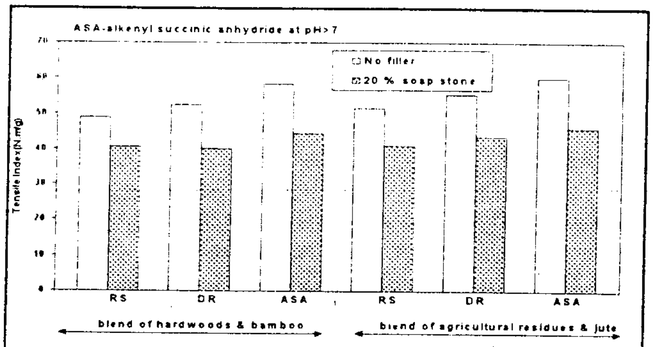

Fig. 2 Effect of sizing with different chemicals on tensile strength
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhdride at pH > 7

make up. In addition, first pass retention must be maximized usually with a cationic polymer or cationic starch addition, to prevent recirculation of the size in the wet end. All these steps will minimize hydrolysis, which can result in poor sizing (7-9). The hydrolyzate can also cause press picking problems because of its tackiness, but its effect can be minimized by employing sufficient aluminum ion at pH greater than 7 (10). An advantage of ASA sizing is that, due to its reactivity, 80-100% of the ultimate effect is achieved while on the machine. This effect allows for good hold-out of size press solution. The historical development of neutral papermaking and development of three main neutral systems have been well reviewed (2,3).

In India there is wide variation in raw material furnishes ranging from mixed hardwoods, bamboo, agro-residues to imported waste paper of Indian and foreign origin. The proper selection of size chemicals and sizing system becomes very difficult for such cases. Most of the mills in India are still following conventional rosin/alum sizing under acidic conditions and only a few have transformed to neutral/alkaline system. Lots of problems are being faced by such mills and, some of these mills have again gone to acidic sizing system after few trials of neutral sizing. The effect of sizing at different pH levels is not well established for indigenous pulps. In the present investigations some of the key differences between rosin based sized and ASA emulsion sized paper with regard to strength, aging and printing characteristics for indigenous raw materials like blend of mixed hardwoods & bamboo pulp (common furnish of Indian large mills) and blend of mixed agricultural residue & jute pulp (common furnish of Indian medium sized mills) have been studied in detail.

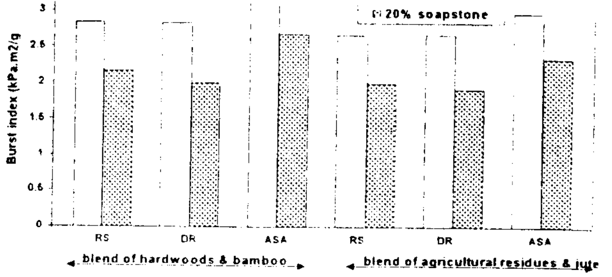

Fig. 3 Effect of sizing with different chemicals on bursting strength
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhdride at pH > 7

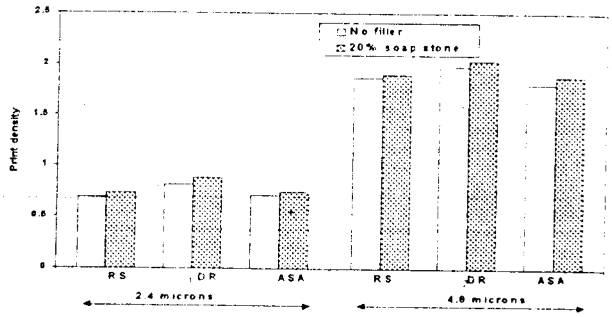

Fig. 4 Effect of sizing with different chemicals on Print density of blend of hardwood & bamboo pulp
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhdride at pH > 7

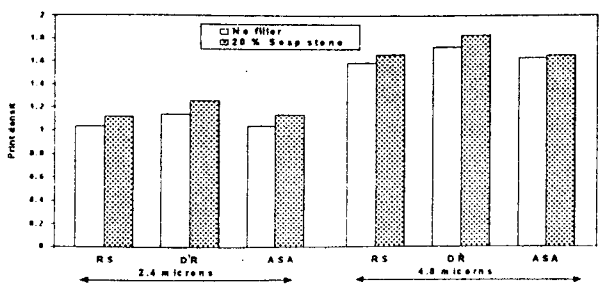

Fig. 5 Effect of sizing with different chemicals on Print density of blend of agricultural residues & Jute pulp
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhdride at pH > 7

RESULTS AND DISCUSSION

Sizing response of different sizing chemicals

Sizing with fortified rosin soap size, dispersed rosin size and ASA emulsion were carried out for blends of bleached mixed hardwoods & bamboo and bleached mixed agricultural residues & jute pulp collected from the paper mills. The sizing with fortified rosin soap was done at acidic pH where as for dispersed rosin and ASA it was at neutral pH. The sizing response of these are shown in Fig 1. There is a marked difference in the sizing response of three different sizes. ASA emulsion develops very good sizing for both pulp blends, followed by dispersed rosin size and fortified rosin soap. At the same dosage of chemicals, the sizing is comparatively lower in agricultural residues than hardwood pulp probably due to the presence of more fines in agricultural residue pulps and higher negative charge (12).

Effect of soap stone filler loading on different sizing chemicals

Fig. 1 shows the effect of filler on sizing with different sizing chemicals. It was found that with the addition of talc as filler the sizing got improved. This is probably due to the low surface energy and hydrophobic nature of soap stone filler. Since sizing phenomenon depends upon the free surface energy of the surface, the soap stone filler adsorbed on the surface of the fiber in the presence of cationic alum lowers the surface energy of the fiber which in turn increases the sizing efficiency of the fiber as shown by the lower cobb values. The decrease in cobb value is more in the case of fortified rosin soap and dispersed rosin size than ASA emulsion size. This is due to the fact that ASA is a chemically reactive size which reacts with cellulose and the presence of filler does not help much with the sizing process, while in case of fortified rosin soap/ dispersed rosin size, both size and filler get adsorbed on the fibre surface physically with the help of alum or any other aluminum containing chemical used in sizing.

These observations can further be explained on the basis of sizing mechanism of rosin soap, dispersed rosin and ASA emulsion. Soap size reacts with alum as soon as it is added to paper stock. Both Electro-static bonding and co-ordinate bonding participate in the reaction, which obviously results in a strong bonded complex. Since alum is able to form ionic and coordinate bonds with the rosin only at acidic pH, sizing with soap size has to be developed in the low pH region. On the other hand, dispersed rosin size consists of rosin acid droplets, which have considerable surface areas. Therefore, its retention is a consequence of colloidal and surface chemistry. Dispersed rosin does not react readily with alum to form aluminum resinate. The alum acts as a bridge between the negatively charged fiber and the negatively charged rosin micelle. In a rosin alum system, rosin in either its free acid or soap form will react with alum to give the aluminum ester products which create hydrophobicity. In the case of soap rosin size under acidic conditions, most of the rosin reacts rapidly with alum in solution to give aluminum ester. In case of dispersed rosin size the reaction of rosin size acid and alum/PAC does not proceed in solution, but occurs on the fiber surfaces in the dryer section. The dispersed rosin size particles are relatively free to migrate during the drying process in the paper web. However as the paper temperature increases on its movement over the drying cylinder, the heat creates a sintering process where the rosin particles melt & distribute uniformly over the surface area of the fibers to form the aluminum resinate (13).

In case of ASA emulsion, the ASA undergoes the reaction of anhydrides. They react with cellulose to form a cellulose ester. This bonded ASA provides sizing at wide pH range when it reaches at the dryer part of the machine. ASA is highly reactive, and the sizing reactions occurs very rapidly but the hydrolysis of the ASA is not desirable since the hydrolyzate is not effective sizing agent and may deteriorate sizing. In excess quantity, it may even destabilize the ASA emulsion (6).

Effect of strength properties on sizing with different chemicals

While comparing the strength properties of two pulps sized with different sizing chemicals under different pH values, it was found that sheets made under alkaline pH conditions were stronger than sheet formed in acidic pH for both mixed hardwoods and mixed agricultural residues pulps. The

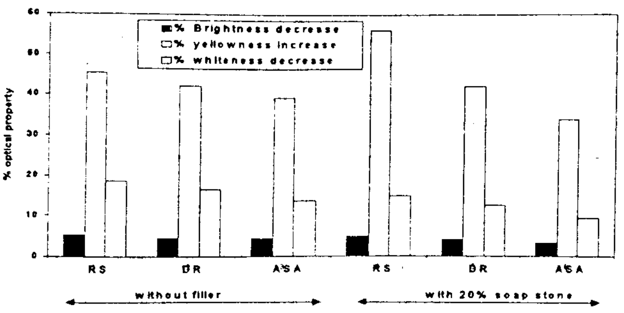

Fig. 6 Effect of sizing with different chemicals on Accelerated aging of blend of hardwood & bamboo pulp
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhydride at pH > 7

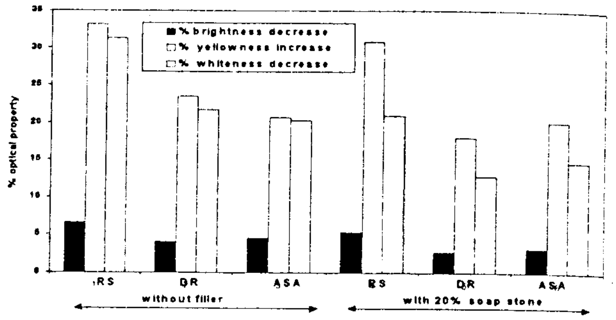

Fig. 7 Effect of sizing with different chemicals on Accelerated aging of blend of agricultral residues & Jute pulp
RS-fortified rosin soap pH 4.5
DR-Dispersed rosin emulsion at pH 6-7
ASA-alkenyl succinic anhydride at pH > 7

tensile index and burst index were on higher side when the sheets were sized with ASA emulsion at neutral pH. The strength properties were comparable both in the case of fortified rosin soap and dispersed rosin. The strength is lower in case of sheets made in acidic pH with rosin soap. The reason for better strength in the case of neutral ASA sized sheets is due to the reason that at higher pH fiber swelling is more which in turn forms stronger bonds and thus making stronger sheet. Additionally the rosin-alum precipitates form bigger aggregates, which interfere in fiber to fiber bonding thus reducing the strength. When the pulps were loaded with 20 % soap stone as filler, the strength properties viz. tensile and burst for both pulps got reduced in comparison to the sheets without filler. At the same filler loading and ash retention, the reduction in strength properties is least in case of paper sized with ASA emulsion under neutral conditions than paper sized with rosin soap at acidic pH conditions Figs. 2 & 3.

Effect on print density on sizing with different chemicals

To study the effect of various sizing chemicals on printing, handsheets were evaluated for print density using IGT printability tester. Printing tests were carried out at two ink layers i.e., 2.4 microns and 4.8 microns . It was observed that for mixed hardwoods pulp, the print density at both ink layers is more in case of handsheets sized with dispersed rosin than ASA. The similar trend was observed for wheat straw pulp Figs. 4 & 5.

The print density of handsheets filled with soap stone, is on higher side as compared to handsheets without filler. Filler particles being smaller in size fill the void volume between the fibers thus providing more smooth surface which results in better printability.

Effect of aging on sizing with different chemicals

To study the effect on optical properties on accelerated aging of the handsheets sized with different sizing chemicals at different pH values, properties like brightness, yellowness, and whiteness of the sheets were measured after aging the handsheets at a relative humidity of 35 % and 400C temperature for 6 hours in Xenoweather fastness tester. There was decrease in brightness and whiteness of the handsheets and increase in yellowness for all the three cases. The percentage reduction in brightness and whiteness and percentage increase in yellowness was maximum in case of rosin soap sized handsheets under acidic conditions. Dispersed rosin at neutral pH has given lesser effect than acidic pH sizing but it is slightly more than ASA. The aging in acidic pH is due to the sulfate and aluminum ions which are free to react with available protons to produce weak acids. Acid hydrolysis is believed to be one chemical reaction resulting in loss of paper permanence (14).

In case of handsheets filled with 20 % soap stone filler, the trend remains the same. Acid rosin soap sized handsheets aged faster than neutral sized handsheets. The effect on the decrease in brightness and whiteness and increase in yellowness was on lower side for filled handsheets Fig. 6 &7.

EXPERIMENTAL

Pulps used in the studies were collected from the near by paper mills. These were bleached pulp blends of mixed hardwood & bamboo and mixed agricultural residues & jute. The sizing was done using

- Fortified rosin soap 0.8 % and 2% alum at pH 4 to 5

- Dispersed rosin 0.8% and 2% PAC at pH 6-7
- ASA emulsion 0.6 % at pH 7.0

Handsheets were made on Rapid Kothen former according to the ISO standard method T06/565N/706. The handsheets were conditioned at temperature 27 10C and relative humidity 65 ? 2% prior to testing.

The accelerated aging of handsheets were done using Xenoweather fastness tester for 6 hours.

The different tests were carried out according to the standards given below:-

Grammage-	ISO 536
Tensile strength-	ISO1924
Bursting strength-	ISO 2758
Brightness-	ISO 2470
Cobb-	ISO 535
Ash content	ISO 2144

Print density- Prints were made using IGT printability tester AIC2-5 at two ink layers i.e. 2.4 and 4.8 micron and print density was measured using Macbeth densitometer.

CONCLUSION

For the pulp blends of mixed hardwoods & bamboo, agricultural residues & jute without any filler, better sizing development is obtained on sizing with 0.6 % ASA emulsion than 0.8% dispersed rosin at neutral pH and 0.8% fortified rosin soap at acidic pH. The extent of sizing development is lower in case of blend of agricultural residues & jute pulp than hardwood & bamboo pulp. This is probably due to the presence of more fines and relatively higher negative charge in the furnish of agricultural residues.

Addition of soap stone as filler helps in improving the sizing to varying extent for both pulp blends in all the cases.

For both the pulp blends the handsheets sized with ASA emulsion under neutral pH gave better bonding properties like tensile strength and bursting strength as compared to handsheets sized under acidic rosin soap and dispersed rosin neutral conditions.

Print quality as assessed by print density at particular ink layer is relatively better for dispersed rosin sized sheets at neutral pH than ASA and fortified rosin sized sheets.

The optical properties reversion is more for acidic sized sheets than ASA and dispersed rosin sized at neutral pH. The best results were obtained for ASA sized sheets. Addition of soap stone as filler helps in reducing the extent of optical properties reversion.

The studies indicate that dispersed rosin with PAC may be the first option for trials of neutral papermaking, followed by reactive sizes.

ACKNOWLEDGEMENT

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The Influence of Paper Sizing on the Amount of Printing Ink Consumed in Offset Printing

This feature reviews an innovative method of determining the influence of the degree of repellency on the amount of ink adsorbed during the printing process. Repellency is expressed by the Cobb$_{60}$ coefficient and wetting time.

The feature establishes relationships between the mass of printing ink remaining of the print and the degree of sizing and other paper parameters such as: fibre and filler composition, sizing, grammage, thickness, apparent density, smoothness, Cobb value, wetting time and ash content.

The knowledge of these relationships will facilitate improved control of the papermaking process, enabling papermakers to engineer papers for their end use.

The papers were printed under standard conditions using a Rolland Practika offset sheet feed press and an IGT apparatus. A cobalt pigment was added to the ink to enable analysis of the ink which is transferred to the paper in very small quantities.

During the chemical analysis on SPECOL, the weight of ink adsorbed by each of the 10 paper samples was determined. To confirm the observations, the concentration of cobalt on the printed papers surface was measured with ICP – MS.

The following conclusion

The idea of the investigation reported in this paper arose in the Polish Security Printing Works (Polska Wytwórnia Papierów Wartosciowych) in Warsaw. In order to impart specific properties to its products the plant uses materials of the utmost quality. This generates high production costs which are reflected in the price of the final product.

In an effort to reduce costs, while producing prints of the highest quality, the prints are often analysed with the aim of determining the influence of the paper base on the results of the printing process on the paper surface.

This paper establishes the relation between the mass of printing ink remaining of the print on one hand and the degree of sizing and other variable parameters characterising the paper on the other. The knowledge of these relationships will enable a better control of the process of paper manufacturing with regard to its end use.

The most difficult stage in developing the experimental methods was connected with the mass of printing ink (M_f) deposited on the paper base during printing, because of the negligible amount of the ink involved. The thickness of the ink layer on the print is roughly 1 μm on average, and it may attain the value of up to 3.5 μm in the flat colour areas spots where a 100% coverage takes place.

The mass of the printing ink transmitted from the printing form onto the paper base is most often calculated by weighing the printing roller of the IGT device before and after the printing process. The difference corresponds to the amount of the ink transferred onto the paper. Hence it is an indirect method for calculating the mass of ink on the print (M_f).

Studies have shown, that this method does not have the precision for gaining the necessary information on the influence of paper parameters on the ink adsorption during printing.

Parameters of Papers Tested

Two main processes take place during the contact of a liquid with paper: the wetting of hydrophilic cellulose fibres and the penetration of the liquid inside the paper structure[1]. The course of these processes depends on:

- the degree of sizing
- method of sizing (internal sizing, surface sizing or both these methods)
- type of sizing agent
- surface structure of paper, its porosity and thickness[2]
- the properties of the liquid, such as viscosity, surface tension etc.[3].

The information on the fibre composition, kind of fillers used, method of sizing and other features of the papers tested are given in *Table 1 (overleaf)*.

A laboratory test with standardised measuring methods was used to determine the essential physico-chemical properties of the papers such as grammage, thickness, apparent density, smoothness, value of Cobb$_{60}$ coefficient, wetting time (this parameter was measured by means of a PDA instrument[4]) and ash content. The values obtained are presented in *Table 2*.

The degree of sizing was determined by two alternative methods: i) the use of Cobb$_{60}$ coefficient[4] and ii) from the wetting time (Max) determined by means of the PDA instrument[5]. The latter value is in direct proportion to the degree of paper hydrophoby and corresponds to the time of paper contact with ink in the printing machine.

The knowledge of the wetting time – which corresponds to the amount of water adsorbed – enables comparison with the amount of ink adsorbed. The time of contact of the liquid medium with the paper surface is similar in both cases.

Preparation of Printing Ink

As mentioned above, the amount of printing ink transmitted onto the paper during printing is very small. It was decided, therefore, to add a certain amount of a pigment containing an element of the series: Fe, Co, Ni, to the colourless ink vehicle. This procedure facili-

was drawn: an increase in the degree of paper repellency is followed by a decrease of ink weight on the surface of the printed papers. Due to other paper properties, this is not a linear relation. The analysis shows significant differences in the degree of ink adsorption between papers with almost the same Cobb$_{60}$ coefficient values.

tates the quantitative analysis of the ink.

When searching for a suitable pigment special attention was called to its chemical properties. A basic criterion of the selection was that the element must not be present in the printing paper used in the experiment – so that the concentration of the metal in analysed samples would correspond only to its content in the ink. It was also necessary to that the pigment is stable at high temperatures, that it can be determined with a high accuracy, and that it is capable of forming a homogenous ink with the vehicle.

All these criteria were met by cobalt, present in the pigment Sicopal* GREEN K9610, produced by BASF. The pigment also contains such elements as nickel, zinc and chromium.

In conformity with the rules of manufacturing printing inks[6], the pigment was used in the amount of 10 % of mass of the ink.

Printing of Papers

In order to obtain as thick a layer of ink as possible, the samples printed had the form of flat colour areas. The papers were printed under standard conditions with the use of:

- IGT apparatus (model C_1),
- offset sheet fed press (Roland Practika).

The use of an IGT apparatus made it possible to obtain thicker ink layers on the print. It should be noted that the thickness obtained is several times higher than the real thickness of the layers obtained in commercial printing processes. The determinations were made using a constant pressure (350 N), constant speed (0.2 m/s) and the amount of ink on the distributing roll was identical for all the samples. The prints on paper strips were made on the screen side and the obtained coloured fields had the dimensions 35 mm x 220 mm.

The papers were also printed on a Roland Practika press at a constant printing speed of

Paper No. (1)	Pulp types used (2)	Fillers used (3)	Additional information (4)
1	coniferous and leafy sulphate cellulose pulp	kaolin	watermark on a part of samples
2	coniferous and leafy sulphate cellulose pulp	kaolin, titanium white	– watermark, – water fixed , – surface sized with modified starch
3	coniferous and leafy sulphate cellulose mass	kaolin	– water fixed, – surface sized with modified starch
4	coniferous sulphate and sulphite cellulose pulp, cotton	kaolin	protective fibres
5	coniferous and leafy sulphate cellulose pulp	kaolin, titanium white	– strongly smoothed, – watermark
6	coniferous sulphate and sulphite cellulose pulp, cotton	dolomite filler	sized with AKD agent
7	coniferous and leafy sulphate cellulose pulp	kaolin	– watermark
8	coniferous sulphate cellulose pulp, cotton	kaolin	-- watermark, – water fixed
9	coniferous and leafy sulphate cellulose pulp	kaolin	– watermark
10	coniferous sulphate cellulose pulp, cotton	titanium white	

Table 1 Characteristics of the papers tested

Paper No. Features		1a with no watermark	1b with watermark	2	3	4	5	6	7	8	9	10
Grammage[g/m²]		74	74	74	74	77	93	150	68	88	77	78
Thickness [mm]		0.112	0.112	0.093	0.086	0.112	0.110	0.207	0.116	0.122	0.116	0.116
Apparent density [g/m³]		0.66	0.66	0.79	0.87	0.69	0.84	0.73	0.59	0.72	0.67	0.68
Smoothness [s]	Felt side	11	11.5	45	50	14	98	12	5	16	12	10
	Screen side	17	17	31.3	31	19	112	16	9	20	16	14
Water adsorption Cobb$_{60}$ [g/m²]	Felt side	31.5	30.6	20.6	21.7	19.6	19.7	22.9	18.6	20	24	21.8
	Screen side	31.4	30.8	20.4	21.6	19.4	22.1	22.9	17.3	19.6	23.1	22.8
Ash content [%]		6	6	6	6	5.4	7	6.3	5.2	5.4	6.4	3.4
Wetting time [s]					0.741	2.782	1.373	0.422	0.995	1.361	0.933	1.025

Table 2 Properties of the papers

5000 sheets a minute. The colour flat areas, printed on the screen side, had the dimensions 25 mm x 40 mm.

The printed samples were divided as a function of the difference in colour and were then subjected to further evaluation.

Evaluation Of Samples In Relation To Colour Difference

From the whole group of prints, the samples selected were those which were undistinguishable by an observer. Where this was impossible, samples most similar to each other in colour were taken.

The colour prints were divided into groups with respect to the printing technique applied and to the colour of the base (white and yellow papers):

- Group 1 – prints made by the IGT apparatus on white papers,
- Group 2 – prints made by the IGT apparatus on yellow papers,
- Group 3 – prints made on the offset Roland Practika press on white papers,
- Group 4 – prints made on the offset Roland Practika press on yellow papers.

The colour of the printing ink was measured with the use of the CIE L*a*b* colour space, in which the differences in colour undistinguishable to the observer constitute a spherical geometric locus having its centre in a previously selected point chosen as a standard[6]. In the present tests the role of standard, see *Table 3*, was played by the sample having the trichromatic coordinates (L*, a*, b*) - the closest to the median of all the coordinates obtained for the given group of papers.

According to the principles of X-Rite Co. in relation to visual perception - shown in *Table 4*[7] - we assumed that the colour difference (vector ΔE^*_{ab}) between the standard and individual sample prints should be ≤ 2. (In the graphical approach to the method, this means that the radius of the sphere having its centre in the point referred to as the standard, is equal to 2).

Some prints failed to meet the accepted criterion. In such cases those prints were chosen, for which the value of the vector ΔE^*_{ab} was least (the least distance between the points and the sphere). The differences in the values of vector ΔE^*_{ab} of the prints did not result from the poor reproducibility of the print, but merely from the colour difference between the printed bases.

A better concordance of the values of this parameter might have been obtained by a change in the mass of the ink applied, depending on the colour of the paper used. In this case, further studies aimed to show adsorption of the ink by different bases under identical printing conditions for each of the papers used would be disqualified.

The graphical approach to the method of sample selection for further analysis is shown in *Figure 1*.

Group No.	L*	a*	b*
Group 1	73.09	-29.61	21.30
Group 2	75.43	-26.43	32.80
Group 3	84.53	-15.81	13.84
Group 4	84.44	-16.70	33.17

Table 3 Standards for all the groups of paper

Paper No.	Ink No.	Absorbance E	Cobalt content C_1 [mg]
1a	2	0.510	0.116
1b	2	0.551	0.200
2	1	1.058	0.239
3	1	0.368	0.084
4	1	0.647	0.234
5	1	0.353	0.122
6	1	0.650	0.245
7	1	0.432	0.147
8	1	0.742	0.286
9	1	0.965	0.386
10	2	0.980	0.221

Table 4 Measurements of printed samples

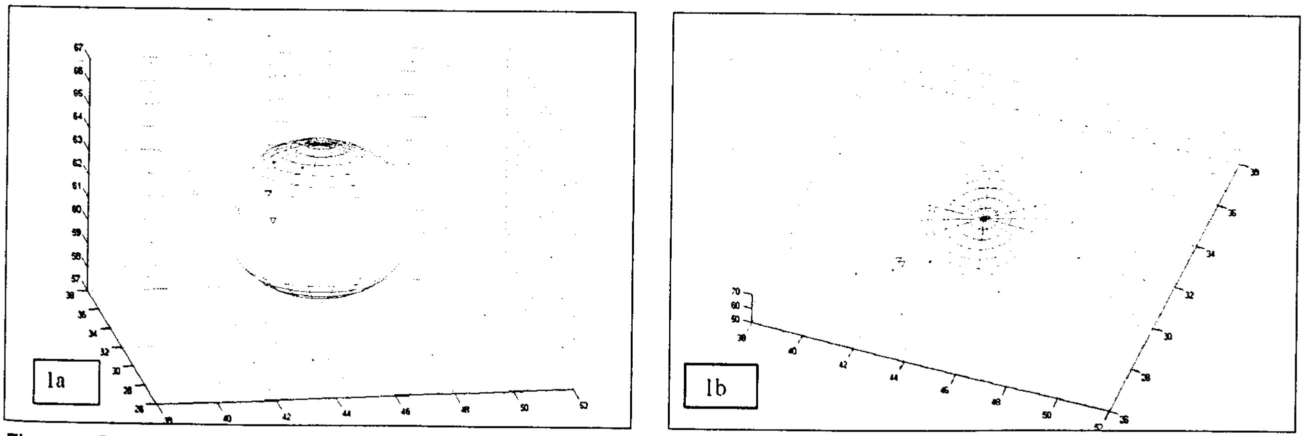

Figure 1 Graphical approach to the method of sample selection based on the colour difference (Group 1 of the papers). Two projections 1a and 1b in the space L*a*b*.

Molecular Spectroscopy Determination of Ink Adsorption

The mass of the ink adsorbed on individual papers printed on the IGT apparatus was determined by spectrophotometric analysis of the content of cobalt. The final result was obtained after a series of several-stage tests.

1. Spectrophotometric determination of cobalt in printed paper samples

The determinations were made on a SPECOL instrument conforming to recommendation of Polish Standards PN – 93/C – 04553[8]. The absorbance values obtained for each sample comprising the printed surface area of $74.55 \cdot 10^{-4}$ m^2 and the corresponding amount of cobalt read on the calibration curve are collected in *Table 4*.

2. Determination of cobalt in the inks

Cobalt was determined spectrophotometrically with the use of a SPECOL instrument conforming to the Polish Standard PN – 86/C – 81549/03[9].

As the amount of ink prepared appeared to be insufficient for printing all the samples, it was necessary to repeat the preparation. An identical ratio of the components used (10:1) was applied, but because of the poor repeatability of this operation, the obtained ink sample was treated as another one and referred to as INK No. 2. The absorbance of the extracts prepared and the content of cobalt in the inks analysed are given in *Table 5*.

Ink No.	Ink sample mass before mineralisation [g]	Absorbance E	Cobalt content specific value
1	1.0790	0.557	0.633
2	4.6217	0.765	0.866

Table 5 Cobalt contents in printing inks

Paper No.	Mass of Cobalt in 1 m^2 of paper x 106 [mg]	Mass of ink Adsorbed by 1m^2 of paper [g]
1a	1.95	2.45
1b	3.36	4.25
2	4.00	5.06
3	1.41	1.79
4	4.08	5.16
5	2.04	2.58
6	4.10	5.19
7	2.47	3.12
8	4.79	6.07
9	6.47	8.18
10	3.71	4.70

Table 6 Adsorption of ink by the papers

The obtained values of C_1 were used for determining the mass of cobalt per 1 g of the inks.

3. Calculation of amount of ink adsorbed

The first step in calculating the amount of ink adsorbed was to find the mass of cobalt contained in 1 g of the ink with the use of the following equation[9]:

$$X = \frac{C \cdot V_0 \cdot 100}{V_1 \cdot m \cdot 10^6}$$

where:

X = mass of cobalt in 1g of the ink [mg],

C = content of cobalt in 1 g of the sample [mg],

V_0 = total volume of the solution [cm^3],

V_1 = aliquot volume taken for analysis [cm^3],

m = mass of ink taken for mineralisation [g].

The calculations gave the following amounts of cobalt in 1g of inks, in:

- INK No.1 – $7.9 \cdot 10^{-6}$ mg,
- INK No.2 – $10.8 \cdot 10^{-6}$ mg.

The precision of the determinations was ±10% in conformity with the standard requirements[9].

After the calculation of cobalt mass in either of the inks tested, the mass of cobalt adsorbed by 1m^2 of each of two the papers was determined.

The mass of cobalt found in the previous calculations (C_1) and corresponding to the mass adsorbed by the print area equal $74.55 \cdot 10^{-4}$m^2 was used to calculate the amount of the metal present on 1m^2 surface of the cellulose product. Next a use was made of the following equation:

$$M = \frac{m_f \cdot a}{b}$$

where:

M = mass of ink adsorbed by 1 m^2 of the paper product [g],

m_f = mass of ink equal to 1g [g],

a = mass of cobalt in 1g of the ink,

b = mass of cobalt adsorbed by 1m^2 of the paper product.

The results of the calculations are presented in *Table 6*.

The Effect of Paper Sizing on the Obtained Mass of Ink Adsorbed

While analysing the process of ink adsorption on the paper surface, it is necessary to take account of the large diversity and multiplicity of factors affecting the described phenomenon. First of all, the following factors should be mentioned:

The papermaking process, and in particular the processes crucial for physical

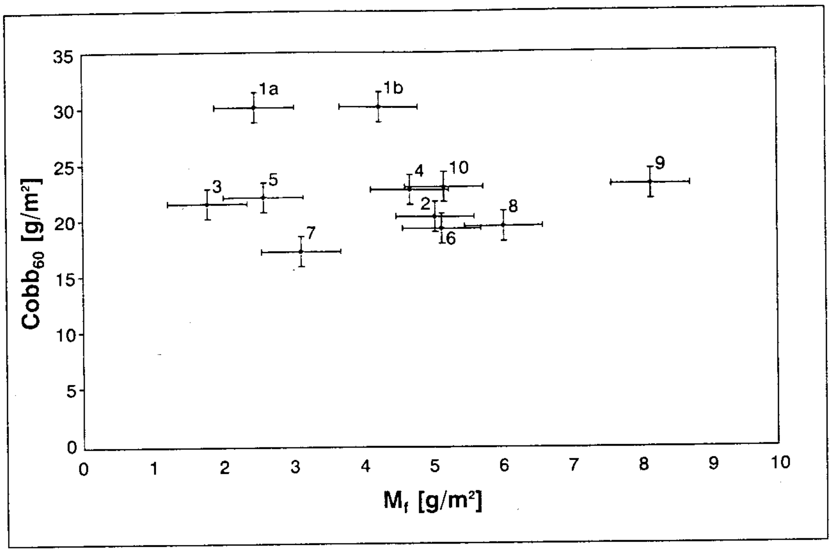

Figure 2 Relation between the amounts of water and ink adsorbed by the papers tested.

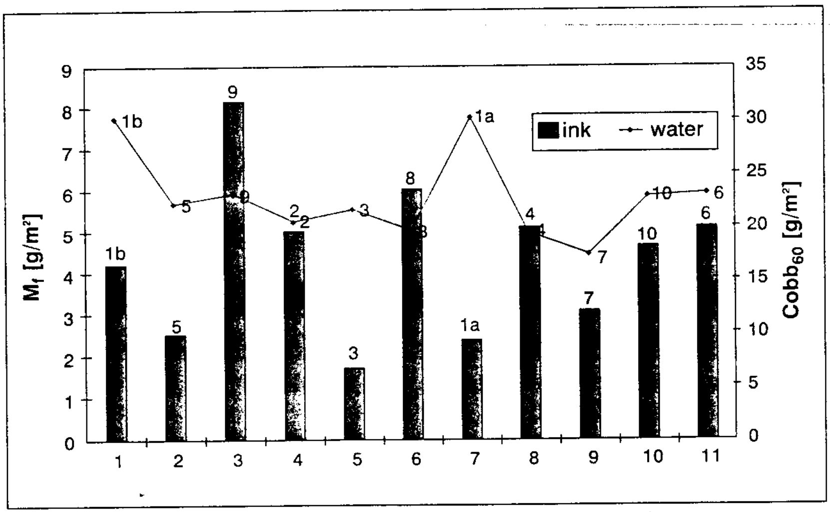

Figure 3 Values of water and ink adsorption by the papers tested.

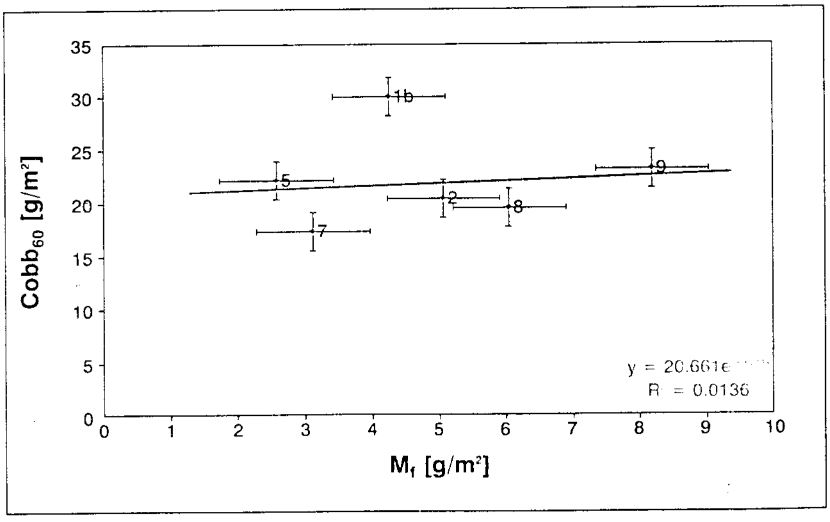

Figure 4 Effect of hydrophobisation degree on the mass of ink adsorbed by papers with no watermark.

properties, and the effectivenes of the sizing process. These factors include:

- The kind and amount of components added to the pulp, such as e.g. the fillers which, if used in excess, reduce the effectiveness of paper hydrophobisation.
- Method of paper sizing and kind of sizing agent used, hence colophony and synthetic agents or, in case of surface sizing, modified starch.
- Degree of paper sizing or degree of its hydrophobisation.
- Fixing the paper with water.
- Presence of watermark.
- Surface smoothness, thickness and grammage of paper.
- Parameters of the ink used, in this work assumed to be identical for all the paper samples[10].

For the sake of the declared goal, both the studies and the discussion of the results obtained have been oriented, first of all, to the determination of the effect of paper sizing on the mass of ink adsorbed M_f.

In most cases, the degree of paper sizing has been considered solely as the parameter affecting the amount of water adsorbed[4]. The observations carried out with this respect have become a basis for further expectations on the amount of ink adsorbed by the paper tested. It has been assumed that proportionality could exist between the amounts of water and ink. Unfortunately, attempts to determine the relationship failed because of the difference in the affinity of water and ink to the hydrophilic cellulose fibres.

Figures 2 – 9 represent a graphical correlation of the values listed in the *Tables 2 and 6*. As can be seen, it is impossible to find a unequivocal answer to the leading question of the analysis in cases, where points corresponding to all the papers tested are present on the figure.

Considerable differences in ink adsorption can be seen between individual papers. *Figure 3* shows that the least values of ink adsorption are observed in the paper of highest smoothness (paper denoted by no. 5) and in the surface sized paper fixed with water (no. 3). One can also see high absorption values obtained for paper no. 9, which deviates highly from the values obtained for other papers, probably because of measuring errors.

The large discrepancies between individual papers can be eliminated by considering smaller groups of papers of similar properties, e.g. papers having no watermark, *Figure 4* or papers of similar surface smoothness. The use of such a procedure gives a more uniform distribution of the characteristic points. It shows also an increase of ink consumption with decreasing sizing degree.

In order to better understand the relationships shown in *Figure 4* it would be advisable to call attention to the points highly differing in position from their neighbours. It becomes evident that paper no. 5 adsorbed a relatively small amount of ink despite the longest wetting time. Such behaviour can be explained by its high surface smoothness (Bekk's smoothness on the printed side of the paper was 112 s.). The "closed" surface of this paper resisted the attack of water strongly thus resulting in increase of the Max value.

The printing ink manifested the same phenomenon by retention of the ink in the outer layer of the base with only slight penetration into the pores. As a result, a correct colour effect of printing was attained with much lesser consumption of the printing ink. The high value of M_f observed for paper no. 6 may be explained by its high thickness (0.207 mm), considerable basis weight (150 g/m^2) and low surface smoothness (16 s).

These observations become most evident in cases where the points belonging to the common approximation curve - *Figures 6 and 7* - are represented as points with coordinates that are arithmetical means of all the values, and the points 5 and 6 remain unchanged and play the role of the characteristic points. In this approach, point 5 corresponds to the paper with the highest surface smoothness, and point 6 correponds to the paper of the highest thickness sized with AKD agent.

In cases where the degree of hydrophobisation is represented as the coefficient Cobb$_{60}$, the mass of ink on the print increases with increasing value of this coefficient, *Figure 6*. The least ink consumption is observed in papers of the lowest surface development, while the highest ink consumption is in the papers of highest thickness and grammage and of low surface smoothness.

The trend line decreases with the degree of hydrophobisation - taken as the time of wetting and measured on a PDA apparatus, *Figure 7*. The cause lies in the specificity of the measurement. The higher the resistance of the paper surface to penetration by the liquid, the higher the observed value of the Max parameter and the lower is the mass of ink adsorbed. The rate of ink migration inside the paper is smaller and one obtains an identical colour effect at a smaller consumption of the printing ink.

The performed measurements also confirm the higher ink consumption by the papers with watermark, *Figure 8*.

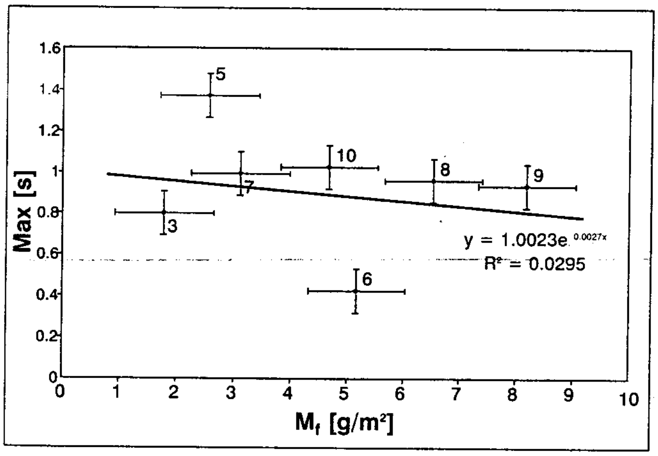

Figure 5 Effect of wetting time on the mount of ink adsorbed.

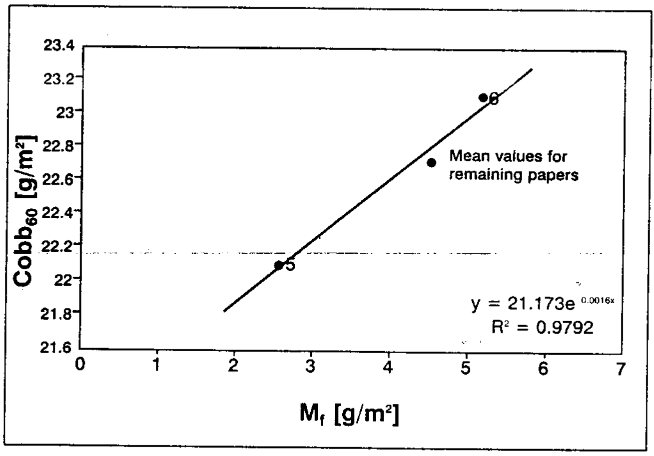

Figure 6 Effect of paper sizing degree (Cobb) on the amount of ink consumed.

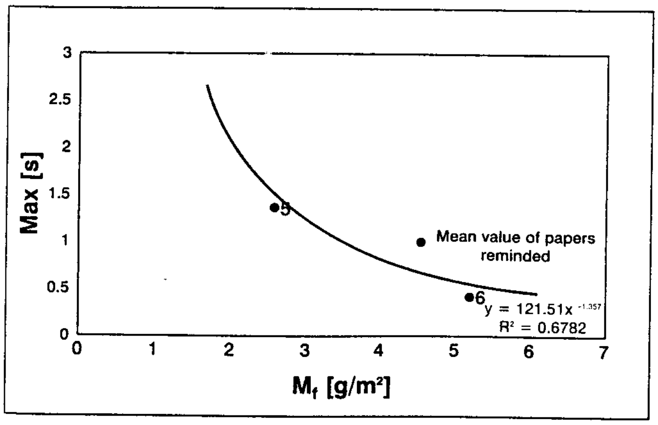

Figure 7 Effect of wetting time on the amount of ink consumed.

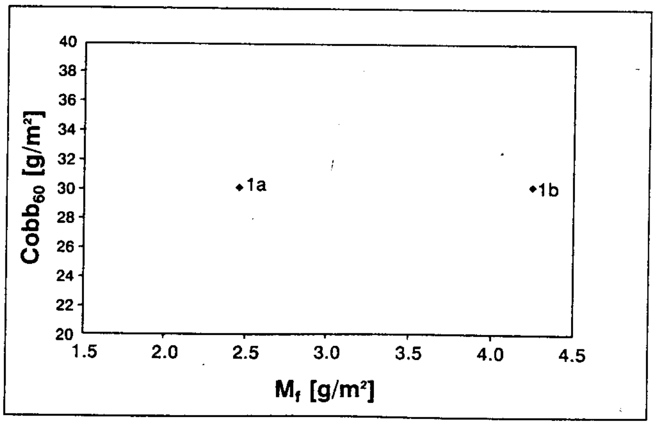

Figure 8 Differences in ink adsorbed by papers 1a and 1b.

The experiments performed also confirm that the Cobb coefficient normally used to estimate the degree of sizing should not be used as an indicator of differences in ink adsorption between the papers tested because of i) the insufficient precision of the $Cobb_{60}$ method and ii) the time of the experiment which differs from the real time of the ink contact with the paper.

As a proof we can quote paper no. 1, which was tested i) as paper no. 1a with no watermark and ii) as paper no. 1b with a watermark. Both papers had similar value of $Cobb_{60}$, which was 31.4 (g/m^2) for 1a and 30.8 (g/m^2) for 1b. However, the corresponding values of M_f were much different, *figure 9* - the value of ink adsorption was nearly twice as high for the watermarked paper.

Determination of Cobalt Concentration Using Icp-Ms Apparatus

In order to confirm the relationships found in the spectrophotometric analysis, the concentration of cobalt was also determined on a mass spectrometer Elan®9000 ICP – MS produced by PerkinElmer™.

In this study, a Q swiched Nd:YAG laser, of frequency quadrupled 266 nm, is focused on a point of the surface studied thus leading to its local evaporation. Owing to the use of laser the analysed surface is very small, 10 - 300 mm in diameter, which increases the accuracy of determination.

The analysed sample is injected, in the form of aerosol, into a plasma – a highly ionised form of matter, where the atoms of elements collide with plasma ions and electrons. The high temperature ranging 600-1000°C, that exists in the electric arc of the instrument, results in excitation and ionisation of molecules, followed by their emission. The emitted particles are analysed by detectors of the spectrometer. Each ion has a strictly defined ratio of mass (expressed as the mass number A) to electric charge (expressed by the number of elementary charges z), owing to which they can be identified and counted[11].

The analyses were carried out on prints made on an offset machine. The aim of the experiment was to determine the content of cobalt isotope ^{59}Co in selected samples. The experiment was divided into four stages depending on the laser energy applied, particle spot diameter, and form of samples used, *Table 7*. This diversification was a result of paper heterogeneity.

The laser spot was sent to the sample surface in 50 millisecond intervals making 40 repetitions for each of three selected points of the sample. The results obtained in the first stage with the use of standard materials normally applied in the analyses involving an Elan®9000 ICP instrument proved to be unacceptable. The failure resulted from insufficient homogeneity of the paper surface,

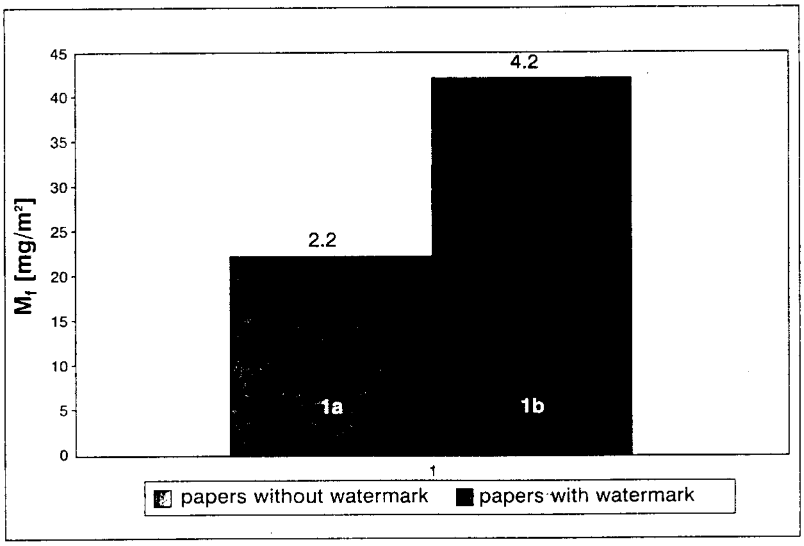

Figure 9 Mean values of ink mass adsorbed by papers 1a and 1b.

Stage	Parameters measured			
	Laser energy		Laser frequency	Spot diameter
	[%]	[mJ]	[Hz]	[μm]
I Low laser spot energy	20	0.48	20	250
II Increased laser spot energy	25	0.6	20	250
III Increased laser spot energy with reduced spot diameter	25	0.6	20	100
IV Increased laser spot energy (incinerated papers analysed)	25	0.6	20	250

Table 7 Parameters of ICP – MS measurements

which caused an excessively large error in the the final result which is the arithmetical mean of all the results.

A higher repeatability of results was obtained by increasing the band energy, owing to which there was an increase in the depth of the surface spot burned out. To reduce the effect of non-homogeneity of the base paper studied, the diameter of the laser beam was reduced.

	Paper no.	Concentration of ^{59}Co [ppm]	Cobb60 [g/m^2]	Max - PDA [%]	Ink mass [mg/m^2]	Apparent density [g/cm^3]
Stage I	1	4400	31.4	*	42.4	0.66
	4	5500	19.4	2.78	51.6	0.69
	6	5700	22.9	0.42	51.9	0.73
	7	11400	17.3	0.10	31.2	0.59
	8	7300	19.6	1.36	60.6	0.72
	9	5300	23.1	0.93	81.8	0.67
Stage II	4	245600	19.4	2.78	51.6	0.69
	7	275900	17.3	0.10	31.2	0.59
	8	301900	19.6	1.36	60.6	0.72
	9	221400	23.1	0.93	81.8	0.67
Stage III	4	838200	19.4	2.78	51.6	0.69
	7	965500	17.3	0.10	31.2	0.59
	8	894900	19.6	1.36	60.6	0.72
	9	1083200	23.1	0.93	81.8	0.67
Stage IV	1	71600	31.4	*	42.5	0.79
	2	75700	20.4	*	50.2	0.84
	5	69900	22.1	1.37	25.8	0.68
	10	67800	22.8	1.03	46.9	0.79
* Papers nos. 1and 2 were not analysed by PDA						

Table 8 Concentration of ^{59}Co found by ICP - MS and other methods

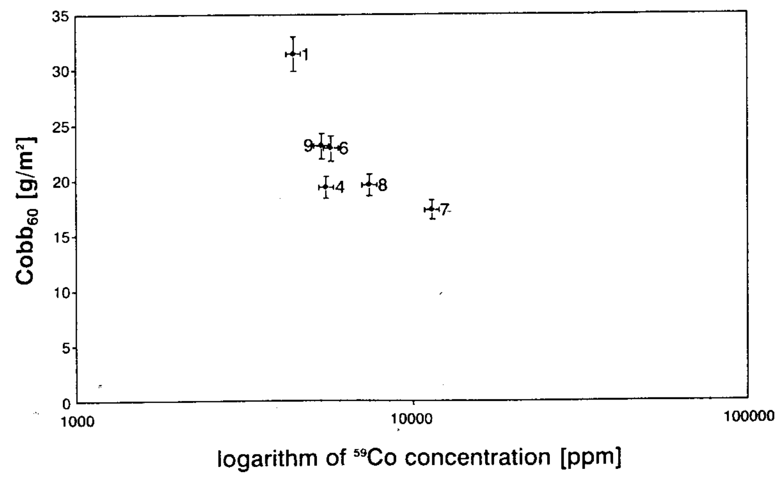

Figure 10 Stage I Effect of hydrophobisation degree determined by Cobb$_{60}$ method of logarithm of ^{59}Co concentration.

In the last stage, the content of ^{59}Co in certain samples was determined in the ashes. In this case, the irradiated object consisted of a single homogenous particle of ash. Owing to such a procedure the final result became independent of the degree of paper surface development.

The concentrations of cobalt found by this method were compared with the following values: Cobb$_{60}$ coefficient; Max coefficient (PDA method); amount of ink adsorbed as determined by SPECOL and with the apparent density of the respective papers, *Table 8*.

No standard of chemical composition corresponding to that of the samples was available during the studies, hence it was impossible to make a calibration curve for the papers tested. An additional error in the results was due to a strong interference of titanium isotope ^{48}Ti, which had been added to the papers. The scope of this interference was not known because of the lack of calibration curve.

For these reasons all the determinations must be treated as semi-quantitative. This makes it possible to provide only an approximate estimation of cobalt concentration in the samples. They can not be regarded as the real quantity of the offset ink adsorbed, but only as a comparative value showing, how the paper properties influence the ink consumption in offset printing.

Graphical presentation of relationships between the parameters mentioned is shown in *Figures 10 - 13*, the axis of cobalt contents being presented in logarithmic scale.

The results of the analysis show that, unlike in the spectrophotometric method, the concentration of cobalt decreases with increasing hydrophobisation of the paper. This phenomenon can be explained in terms of the specificity of the ICP-MS analysis. The laser spot impinging on the paper sample was able to penetrate merely the outer layer of the paper base, along with the layer of ink deposited - because of the microscopic dimensions of the analysed surface which are of the order of 100 and 250 μm.

A consideration of the paper properties showed, that the more sized and the more homogenous the paper surface, the more pigment containing cobalt remained in the outer layer of the sample (on the paper surface). These relationships are shown in *Figure 12*, where the amount of ink determined by the SPECOL instrument is in inverse proportion to the logarithm of concentration of the ^{59}Co isotope determined by means of the Elan®9000 ICP – MS instrument.

Analyses of the ashes obtained by incineration of the printed papers gave the results which were the closest to those obtained by the colorimetric methods. The amount of cobalt in the samples increased with decreasing degree of hydrophobisation, *Figure 1*.

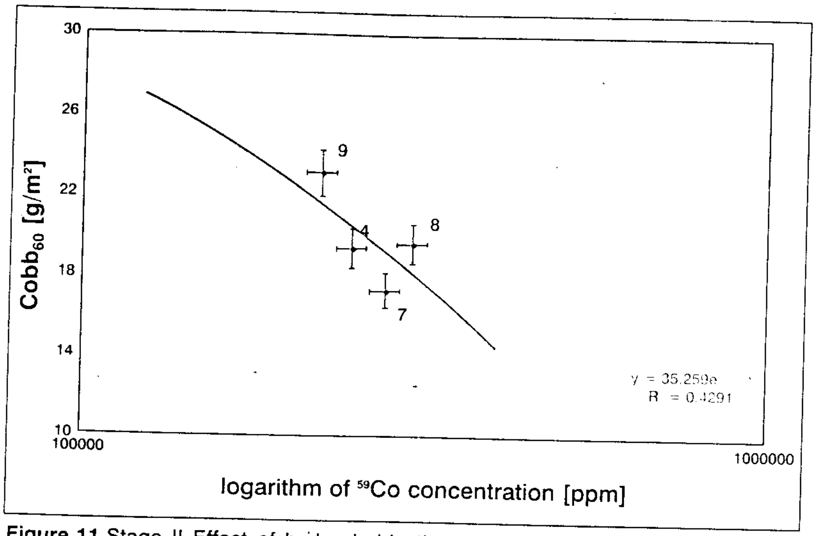

Figure 11 Stage II Effect of hydrophobisation degree determined by the Cobb_{60} method on logarithm of ^{59}Co concentration.

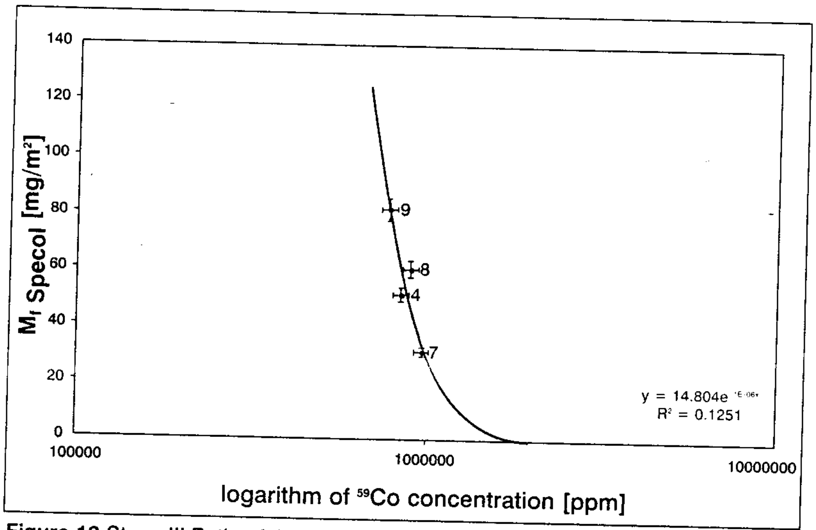

Figure 12 Stage III Ratio of the amount of ink adsorbed by paper during printing on offset machine to the logarithm of ^{59}Co concentration.

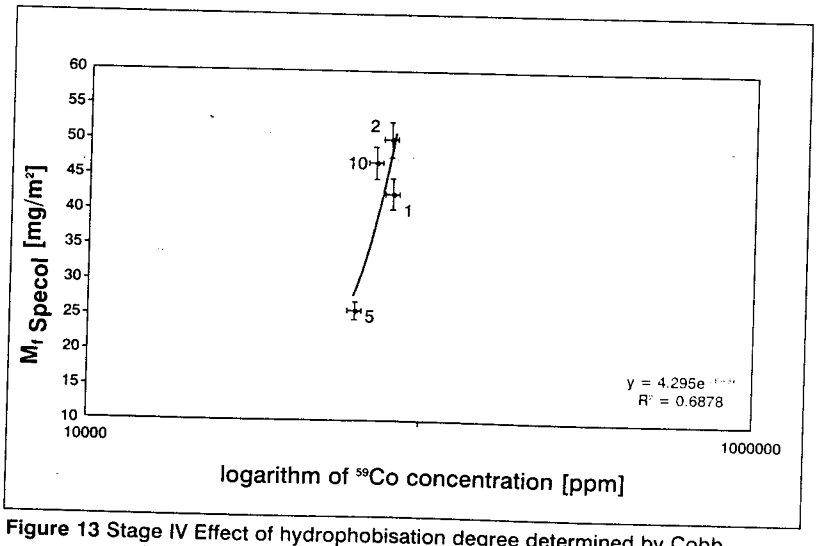

Figure 13 Stage IV Effect of hydrophobisation degree determined by Cobb_{60} method on logarithm of ^{59}Co concentration.

Conclusions

The multistage analysis consisting of:

- determination of hydrophobisation degree of the papers tested,
- preparation of printing ink containing definite amounts of cobalt added,
- offset printing of papers on an IGT device and on a Roland Practica press,
- determination of the mass of ink deposited on print samples, which were the closest to each other with respect to the colour obtained, led to the following conclusions:

1) The amount of printing inks consummed by the paper base increased with the decreasing degree of paper hydrophobisation. The relation was not linear, because of the diversity of the variables involved (to avoid diversity of results the differences between the papers analysed should not go beyond the degree of sizing);

2) Among the papers with an identical degree of hydrophobisation, the least amount of printing ink was adsorbed by the papers characterised by the highest surface smoothness. The following relationship is evident: the more compact the surface of the paper, the less ink migrated to the deeper layers and the less ink was necessary to obtain a definite colour effect of the print;

3) Among papers of identical sizing degree, the most ink was adsorbed by the paper of the highest basis weight and the highest thickness;

4) Watermarked papers with watermark were characterised by higher consumption of printing ink;

5) Papers with an identical sizing degree, determined by the Cobb_{60} method, exhibited various ink adsorption. It is worth mentioning that the Cobb_{60} coefficient had similar values for both No 1a and No 1b papers. As a consequence of the latter, the use of this criterion for the consumption of ink by the paper would give the values which differ greatly from the real ones;

6) In the studies performed, the behaviour of the papers was analysed as the effect of action of two media of very different affinity to cellulose fibres. This fact was particularly evident in the analysis of paper smoothness, which had no decisive effect on water adsorption, but it did have a strong influence on the mass of ink necessary to obtain a predetermined colour effect.

This method of determining the mass of ink deposited on the print was never used before. One of the most important advantages of this method is, that it can be used in all cases where it is necessary to determine precisely the ink consumption during printing - not only on the IGT apparatus – the use up to this point - but also under industrial conditions.

Such information is particularly important for printing houses using expensive or very expensive printing inks with special properties. Such printing houses can use the tests of ink consumption described in this work to choose a paper of the lowest ink adsorption while maintaining satisfactory printing quality. The low cost of the study with the aid of SPECOL spectrophotometer and the high accuracy of the method are also worth of mentioning.

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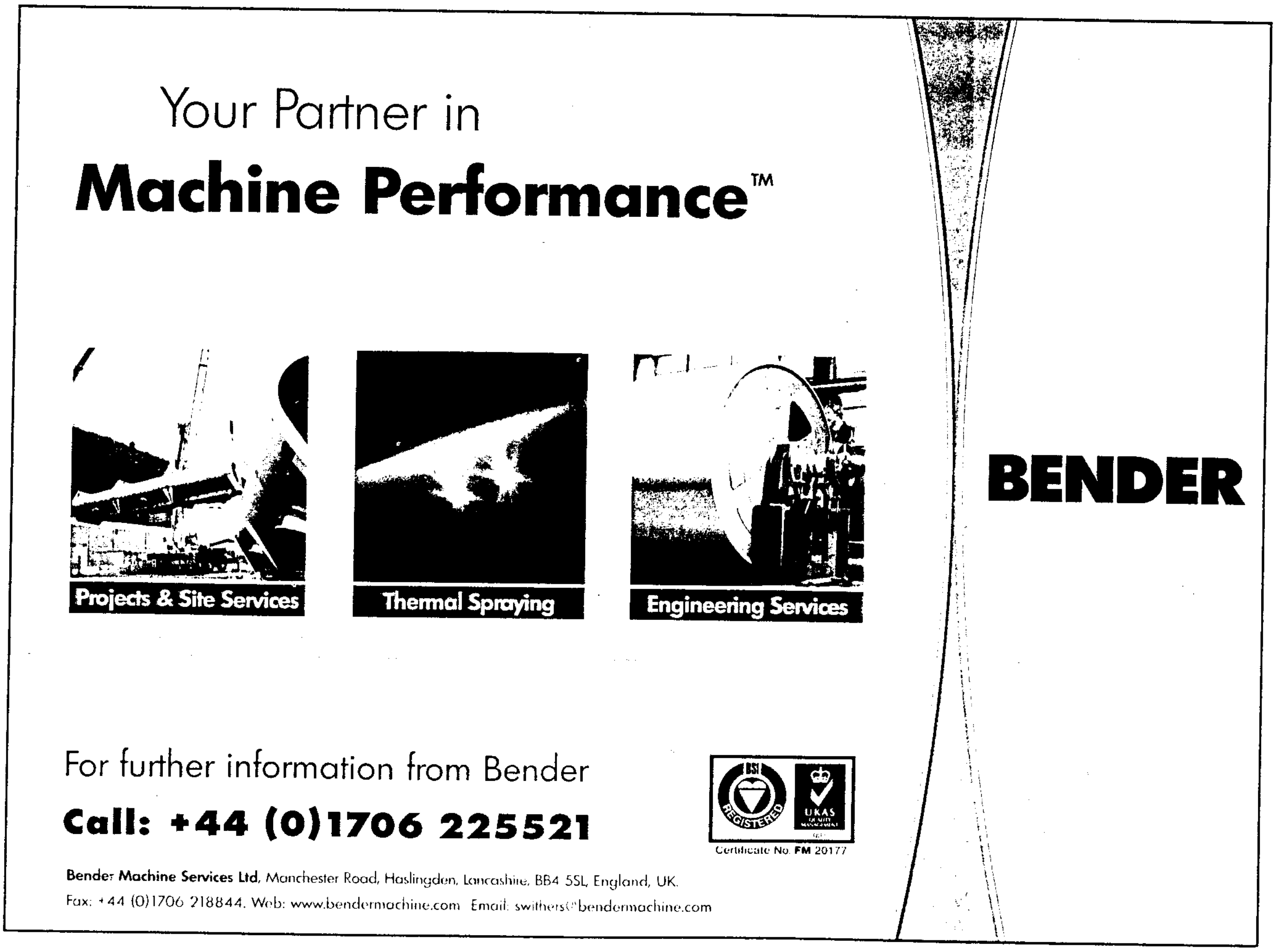

Surface Characteristics and Sizing Response of Paper Sheets Sized by Anionic Emulsion of Fatty Acids

H. YAMAMOTO, T. KITAOKA and H. TANAKA

The surface characteristics of paper sheets tub sized with anionic emulsion size consisting of fatty acids were investigated for the mechanism of sizing response by the combined use of X-ray photoelectron spectroscopy and pyrolysis gas chromatography. The atomic ratio of fatty acid-derived carbons to cellulosic ones, indicating the surface abundance of hydrophobic size components on hydrophilic paper sheets, well reflected the sizing response that was not attributed to the size content of the paper sheets. The aluminum components on the fibre surfaces must behave as an inhibitor for the undesirable aggregation of size components themselves and, as a result, contribute to the remarkable enhancement of sizing effects.

Les caractéristiques de la surface des feuilles de papier encollées en cuve avec une colle d'émulsion anionique consistant en acides gras ont été étudiées dans le contexte de l'encollage en combinant la spectroscopie XPS et la chromatographie à pyrolyse. Le rapport atomique des carbones dérivés des acides gras et des carbones cellulosiques, qui indique l'abondance en surface des éléments de colle hydrophobe sur les feuilles de papier hydrophiles, reflète la réponse de l'encollage non attribuable à la teneur en colle des feuilles de papier. Les éléments aluminium sur la surface des fibres doivent agir comme un inhibiteur de l'agrégation indésirable des éléments de colle mêmes, et contribuent ainsi à l'amélioration remarquable des effets de l'encollage.

INTRODUCTION

Paper sizing gives rise to a drastic change in the surface characteristics of paper sheets for liquid absorptive and resistant properties by a simple technique whereby hydrophobic sizing agents are added to paper stock or subjected to the surface treatment of dried paper sheets. This is of great interest and of great significance from the point of view of the functional design of cellulosic fibre materials. Internal rosin emulsion sizing systems, with aluminum sulphate (alum) as a retention aid at the wet end, have been applied widely to practical papermaking processes, and thus many investigations about rosin-related sizing mechanisms have been reported [1–5]. Recently, surface sizing with emulsion sizes has attracted attention since wet-end management is difficult in terms of sizing effectiveness due to the utilization of recycled pulp fibres of poor quality and the accumulation of various interfering substances by mill system closure. Thus, the mechanisms and applications of surface sizing with emulsion sizes are regarded as being of major importance in effective paper sizing.

Surface-sizing systems with synthetic polymers have been reported [6]. However, they appear more similar to coating treatments than to conventional sizing procedures. A few studies have been carried out with regard to surface sizing with soap rosin sizes [7] and alkylketene dimers [8,9] for comparing their internal sizing mechanisms. In our previous studies, several findings for surface sizing with emulsion sizes containing rosin or fatty acids have been reported:

— Tub sizing with rosin emulsion required the internal addition of a cationic additive, not being limited to alum, for good sizing appearance [10]; and

— Most size components in alum-treated paper sheets by fatty acid-sizing remained free without the formation of any aluminum salts [11].

Scanning electron microscopic (SEM) observations and two-dimensional X-ray photoelectron spectroscopic (XPS) analysis of the surfaces of tub-sized sheets implied that the higher sizing efficiency was induced by the more uniform and stable size distribution on the fibre surfaces [10,11]. However, it is not clear yet why cationic additive-free paper, into which plenty of size emulsions are introduced, cannot demonstrate sizing effects, and how the aluminum components originating from alum contribute to the sizing appearance.

In this study, the surface characterization of paper sheets tub-sized with an anionic emulsion size consisting of stearic and palmitic acids was carried out by the combined use of XPS analysis and pyrolysis gas chromatography (PyGC). The sizing efficiency of the tub-sized sheets was investigated by comparing the surface abundance of the size components with the total size content when the alum addition levels varied in the base sheetmaking. Fatty acids having alkyl and carboxyl groups were allowed to be applied as model components of rosin acids [5,11,12]. The XPS/PyGC comparative analysis was established in our previous study for evaluating the sizing effect against size content [13]. The factors influencing the sizing

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response and the roles of the aluminum components in the sizing appearance are discussed on the basis of the results obtained through the XPS/PyGC comparative analysis.

EXPERIMENTAL

Materials

A commercial hardwood bleached kraft pulp (HBKP) was beaten to 460 mL Canadian Standard Freeness [14] with a Hollander beater [15]. The fraction of fibre fines in the beaten HBKP was removed by filtration five times with a 200-mesh single screen [16]. A fatty acid mixture consisting of stearic and palmitic acids (Wako Pure Chemical Industries Co., Osaka, Japan) and poly(oxy-1, 2-ethanediyl), α-sulpho-ω-(4-nonylphenoxy)-, sodium salt (RB-330, Daochuang Chemical Co., Henan, China) were used as the size components, and an anionic emulsifier for preparing an anionic emulsion size, respectively. Alum ($Al_2(SO_4)_3$) and other chemicals were reagent grade (Wako Pure Chemical Industries Co., Japan).

Preparation of Anionic Emulsion Size

A mixture of stearic and palmitic acids with an equal weight ratio was suspended in deionized water with a 0.125–4.0% (wt/wt) consistency, and an RB-330 anionic emulsifier (10% on total weight of size mixture) was added to the suspension, followed by boiling for 5 min. After the size components melted, the suspension was emulsified by ultrasonication at room temperature for 1 min, and immediately cooled in an ice bath. The emulsified solutions obtained were gravimetrically adjusted to a designated concentration: 0.125, 0.25, 0.50, 1.0, 2.0 or 4.0% (wt/wt). The zeta-potential value and average particle size of the anionic emulsion size were measured using a laser doppler electrophoresis type zeta meter equipped with a photon correlation spectroscopy-type particle size meter (Zetasizer 3000, Malvern Instruments Co., Malvern, UK), and are listed in Table I.

Base Sheetmaking and Tub-Sizing Procedure

The designated amounts of alum (0–2.0% on dry weight of pulp) were added to a 0.15% fines-free pulp suspension that had been adjusted to pH 6.5 with a dilute HCl solution. Base sheets with a basis weight of 60 g/m^2 were prepared from the suspension according to the TAPPI Test Method T 205 [17]. After wet pressing, the handsheets were air dried with restraint at 23°C and 50% RH for more than 24 h, and were subjected to the tub-sizing procedure. The handsheets were dipped in a 0.125–4.0% (wt/wt) size emulsion for 1 min, and the wet sheets, picked up carefully on a metal plate with a pair of tweezers, were superposed with three blotting papers (No. 2, Advantec Toyo Co., Tokyo, Japan). Then, the assembly was pressed at 3.5 kg/cm^2 for 5 min and placed under conditions of 23°C and 50% RH for more than 24 h. Parts of the tub-sized sheets were thermally treated at 105°C for 20 min, and conditioned again at 23°C and 50% RH for more than 24 h.

Quantification of Total Size Content by PyGC

The total amounts of the size components in the sheets were determined quantitatively by PyGC with an online methylation technique [1,18]. A handsheet sample (~0.5 mg) was set in a small platinum pot, followed by the addition of 1.0 µL of a 25% tetramethylammonium hydroxide/methanol solution. The sample was pyrolyzed for gasification and methylation of the sample components at 450°C under the flow of helium gas by a vertical microfurnace-type pyrolyzer (PYR-4A, Shimadzu Co., Kyoto, Japan), which was directly attached to the GC apparatus (GC-17A, Shimadzu Co., Japan). Amounts of size components in handsheets, mg/g of a paper sheet, were calculated on the basis of peak areas due to size components in the PyGC profiles using a calibration curve prepared beforehand. The deviations of size content obtained by this PyGC method were ±3% for each sample.

Surface Size Abundance Determined by XPS

The surface characterization of the tub-sized sheets was carried out using an XPS apparatus (AXIS-HSi, Shimadzu/Kratos Co., Kyoto, Japan). High-resolution XPS spectra were obtained using a monochromatic Al Kα X-ray source (1486.6 eV) at a voltage of 15 kV and a current of 10 mA at an operating pressure of below 5 × 10^{-7} Pa. The pass energy and step width in the detection of photoelectrons were set at 10 and 0.05 eV, respectively. The binding energies of all spectra were related to a conspicuous C1s signal (unoxidized C–C band) at 285 eV [10,13]. The atomic ratio of carbon of size origin to carbon of cellulose origin, indicating the surface abundance of the size components present on the pulp fibres, was defined by dividing the amounts of unoxidized and carbonyl carbons by those of C–O and O–C–O originating from cellulose. The unoxidized carbons from hydrocarbon contaminants, inherently existing on the HBKP sheets without any additives, were dealt with as a background [13]. Thus, the relative values obtained through XPS analysis mean exactly the surface hydrocarbon fraction, being closely related to the surface size abundance.

Other Analyses

The sizing levels of the tub-sized paper sheets were evaluated using the Stöckigt sizing test, where 2% NH_4SCN and 1% $FeCl_3$ were used for the penetration test in the z direction of the paper sheet, and the colorimetric change from light yellow to deep red was detected visually [19]. In general, soft-sized paper sheets have Stöckigt sizing degrees of +0–10 s, and hard-sized ones of more than 30 s. The SEM observation of the surfaces of the tub-sized sheets was performed in an SEM apparatus (JSM-5600, JEOL Co., Tokyo, Japan) at an electron accelerating voltage of 5 kV after gold coating (JFC-1100, JEOL CO., Tokyo, Japan).

RESULTS AND DISCUSSION

Correlation of Various Sizing Parameters of Tub-Sized Sheets

Figure 1 shows the relationships among the sizing features, the atomic ratios of carbon implying the surface abundance of size components, and the size content of the tub-sized paper sheets with an anionic emulsion size of 0.25% (wt/wt). The base sheets for tub sizing were prepared from fines-free pulp with 0–2.0% alum to exclude the possibility that the alum addition level brought about the difference in the retention of the fibre fines, possibly resulting in changing the structural properties of the paper sheets and their sizing behaviour.

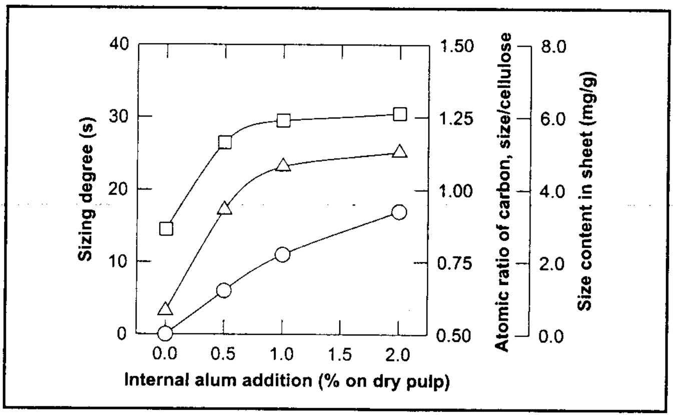

Fig. 1. Sizing degree (○), atomic ratio of carbon (△) and size content (□) of handsheets tub sized with 0.25% (wt/wt) emulsion size. Handsheets were prepared beforehand with 0–2.0% alum.

TABLE I
ZETA-POTENTIALS AND AVERAGE PARTICLE SIZES OF COMMERCIAL ROSIN EMULSION AND HANDMADE EMULSION

	Zeta-potential (mV)	Average particle size (nm)
Commercial emulsion rosin size (AL-120)*	–50.8	178
Emulsion size prepared of fatty acids	–55.4	320

*The commercial sizing agent was kindly provided by Japan PMC Co., Tokyo, Japan.

The sizing degrees of the tub-sized sheets increased with increasing alum addition in the base sheetmaking. Both the size content of the sheets and the atomic ratio of carbon on the sheet surfaces also increased.

The emulsion size prepared in this study had a negative charge of ~–50 mV, similar to the commercial rosin emulsion size, as shown in Table I. The increase in size retention may have occurred by the attraction between anionic size emulsions and the aluminum components with a positive charge partially recovered in the aqueous sizing process [11]. The atomic ratio of carbon, in the surface hydrocarbon fraction determined by XPS, indicated the relative abundance of the size components on the sheet surfaces, and reflected well the sizing features of the sheets. These results appeared reasonable. However, it was reported in our previous studies that most rosin components in the sheets with good sizing effects were free acids [2], but that the rosin acid emulsions in the alum-free handsheets had nearly no effect on the sizing appearance [10]. Thus, the poor sizing behaviour of alum-free sheets must not be attributed to the chemical structure and the content of the size components. A detailed investigation into the roles of the aluminum components in surface sizing with emulsion size was carried out by XPS/PyGC comparative analysis that had been applied to account for the sizing characteristics independent of the size content in a model sizing system with a nonaqueous solvent [13].

Figure 2 displays the characteristic sizing parameters: the sizing degrees of the tub-sized sheets; the hydrocarbon fractions on the surfaces and the total size content. A clear sizing response was observed only when a 2.0% alum-treated base sheet (A) was tub sized. An alum-free sheet (B) with a size content nearly equal to sheet (A) exhibited no sizing effect. Furthermore, even twice the amount of size components as that of sheet (A) made no contribution to the sizing appearance, as shown in a tub-sized alum-free sheet (C) using a size emulsion with four times the concentration of that in sheet (A).

In surface-sizing systems, the retention level of the size components in a paper sheet is adjusted readily by controlling the concentration of the size solution [10]. However, the higher size content of alum-free sheets (B) and (C) did not always result in a higher sizing effect. On the other hand, the atomic ratio of carbon on the alum-treated sheet (A) was appreciably higher than those on sheets (B) and (C). This reflected the sizing phenomenon well.

The atomic ratio of carbon, the size-related carbons/cellulose-related carbons, means the abundance of size components on the tub-sized surfaces, although the size content of the sheets was not related to their surface hydrocarbon fractions. These results indicated that the atomic ratio of carbon obtained through XPS analysis is superior to the conventional size content as a sizing parameter directly reflecting the sizing effect. The XPS can detect only photoelectrons from superficial elements of a specimen. Thus, detectable amounts of carbonic atoms originating from the size components must depend on the states of the size aggregation on the sheet surfaces. The XPS/PyGC comparative analysis presumably suggests that the size components on sheet (A) were not localized horizontally compared to those on sheets (B) and (C), and that some attraction acting between the size and aluminum components behave as an inhibitor for the characteristic size aggregation.

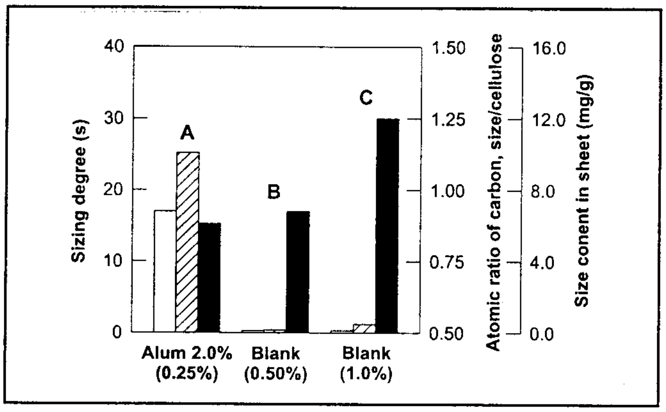

Fig. 2. Sizing degree (open bars), atomic ratio of carbon (striped bars) and size content (filled bars) of handsheets tub sized with 0.25–1.0% (wt/wt) emulsion sizes. Handsheets were prepared beforehand either with 2.0% alum or without alum.

SEM Observation of the Surfaces of Tub-Sized Sheets

Figure 3 illustrates the SEM images of the surfaces of paper sheets, tub sized with an anionic emulsion size, when the base sheets were prepared (A) with or (B) without alum. The total size content of sheets (A) and (B) was almost the same. However, distinct differences in the sizes of the particles were observed. Only small particles were scattered on the surfaces of the alum-treated sheet, as shown in Fig. 3A, although huge lumps of more than 10 μm in diameter were located in the limited regions of the alum-free sheet surfaces, as shown in Fig. 3B. From the SEM result alone, the massive pieces of matter in Fig. 3B cannot be identified accurately. However, it was supposed that they were agglomerates of size emulsions since there was no such mass on the surface of the paper sheets without tub sizing. Several small particles in alum-treated sheets were collapsed at room temperature, originating from spherical particles of ~320 nm in diameter, as listed in Table I. These size particles were present everywhere on the surfaces of the tub-sized sheets containing aluminum components. However, in

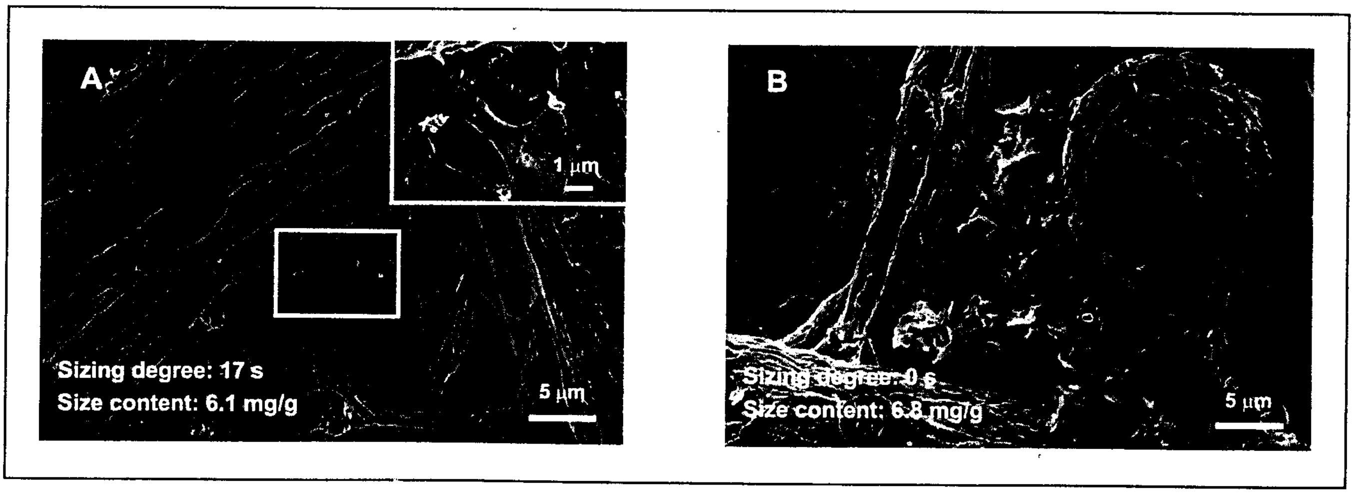

Fig. 3. SEM images of the surfaces of tub-sized sheets (A) and (B) as indicated in Fig. 2. An inset is the magnified image of an outlined region of the sheet (A).

contrast, similar particles were absent from the alum-free sheets, and only massive particles were found.

The SEM results suggested that the aluminum components from the alum possibly contributed to the distribution of the size components on the sheet surfaces, and supported the results obtained through the XPS analysis. The measurement range of the XPS analysis is a sample surface of 0.8 mm in diameter. Thus, it is significantly larger than that of the SEM analysis shown in Fig. 3. Therefore, XPS/PyGC comparative analysis would be a useful, superior method for quantitatively determining the aggregation states of size emulsions on paper sheets because it avoids the miscellaneous factors given through the arbitrary choice of SEM observation points.

Effects of Curing Treatment on Sizing Efficiency

Figure 4 displays the sizing effect and the surface atomic ratio of the size-related carbon of air-dried and cured handsheets after tub sizing with an emulsion size of 0.25% (wt/wt). Nearly no effects of thermal treatment at 105°C for 20 min appeared in the alum-free sheet whereas, in the sheets containing aluminum components, both the sizing degrees and the atomic ratios increased significantly by curing treatment. It was confirmed that the size content in paper sheets remained unchanged from before to after the curing treatment (data not shown). Thus, these atomic ratios indicated that the abundance ratios of the size components on the sheet surfaces correspond precisely to the sizing efficiency.

Table II compares the differences in the sizing degrees and the surface C atomic ratios of alum-free sheets with those of alum-treated sheets after tub sizing with emulsion sizes of various concentrations. An interesting, drastic change in the atomic ratios and resulting sizing enhancement were obtained only in the alum-treated sheets, regardless of the size concentration. These phenomena therefore must be induced by direct interaction of the aluminum components with the size constituents consisting of a fatty acid mixture with a melting point of ~64°C [5] once melted and then deposited.

In a model system of fatty acid/$CHCl_3$ sizing, the XPS/PyGC comparative analysis suggested that the aluminum components in the base sheets stably placed the hydrophobic size components on the hydrophilic paper surfaces by reversible interfacial interaction acting between the fatty acids and the aluminum components [13]. Sufficient thermal treatment would destroy the size emulsions in the sheets, and the molten size components spread temporarily over the fibre surfaces. Then, the quantity of size molecules that interacted with the aluminum components in the alum-treated sheets increased under thermal treatment and thus the surface atomic ratios of carbon increased markedly. On the other hand, an attractive force anchoring the size molecules onto the cellulose substrate was never achieved in alum-free sheets containing plenty of size components, and the self-assembling phenomenon of size molecules possibly occurred in a similar way to that shown in Fig. 3B. Therefore, the sizing response, which means the sizing effect in terms of the size content, was enhanced only in the alum-treated sheets by curing treatment.

Additive Balance for Effective Sizing Response

The aluminum components in the base paper sheets for tub sizing with emulsion-type fatty acid sizes must play an important role in scattering the hydrophobic sizes on the paper surfaces. However, it was not clear what amounts of aluminum components were required to induce a good sizing appearance. Figure 5 shows the sizing behaviour and sizing parameters of 2.0% alum-treated sheets by tub sizing with emulsion sizes of 0–4.0%. The size content of these sheets increased approximately in proportion to the size concentration, while the size components were introduced forcibly into the paper sheet. However, there was a significant leap in the sizing effect with an increase in the size concentration up to 1.0% (wt/wt), whereas a drastic drop in the effect was observed in higher size concentrations over 1.0%. Thus, these sizing phenomena could never be accounted for by the size-retention behaviour.

The surface hydrocarbon fractions clearly increased as the concentrations of the size solution were increased, reflecting sizing enhancement, and then became a plateau at size concentrations more than 1.0%. The characteristic behaviour of the sizing response and sizing parameters strongly suggests that the excess size components caused the relative insufficiency of aluminum species on fibre surfaces and the resulting ineffectiveness in the sizing appearance, possibly because the aggregation of the size components themselves occurred prior to interfacial action between size emulsions and aluminum components. The size concentration inducing the maximum sizing effect decreased with a decrease in the alum addition levels (data not shown). An excess of internal

TABLE II
SIZING DEGREES AND ATOMIC RATIOS OF CARBON OF HANDSHEETS SIZED WITH 0.25–1.0% (wt/wt) EMULSION SIZES

Alum (% on dry pulp)	Size concentration (%)	Sizing degree (s)		Atomic ratio of carbon	
		Air dried	Cured	Air dried	Cured
0.0	0.25	0	0	0.58	0.55
0.0	0.50	0	0	0.51	0.58
0.0	1.0	0	0	0.53	0.69
2.0	0.25	17	36	1.1	1.4
2.0	0.50	20	38	1.9	3.1
2.0	1.0	26	48	2.6	3.5

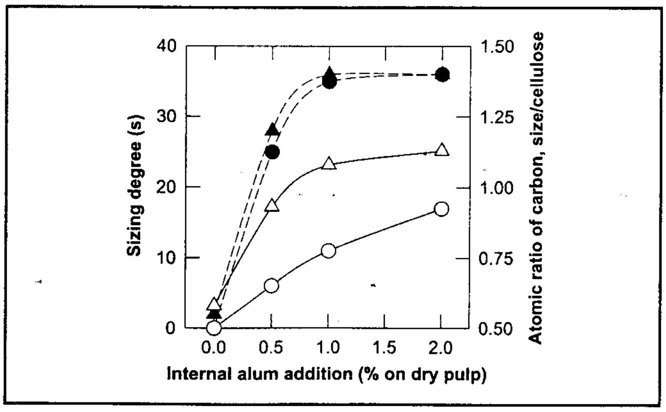

Fig. 4. Sizing degree (○,●) and atomic ratio of carbon (△,▲) of handsheets sized with 0.25% (wt/wt) emulsion size. Solid lines: air dried; dashed lines: cured. Handsheets were prepared beforehand with 0–2.0% alum.

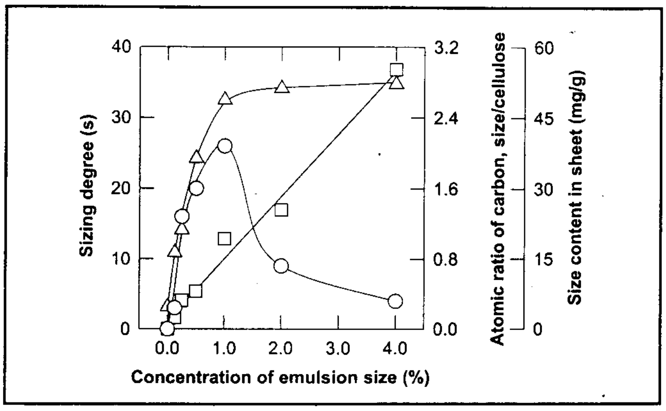

Fig. 5. Sizing degree (○), atomic ratio of carbon (△) and size content (□) of handsheets sized with 0–4.0% (wt/wt) emulsion sizes. All tub-sized sheets were air dried without any thermal treatment. Handsheets were prepared beforehand with 2.0% alum.

alum addition brought about the remarkable coagulation of aluminum components on the fibre surfaces [20] and the sizing tendency became unclear.

The constant atomic ratios of carbon in the tub sizing system with the concentrated size emulsions were attributed to the overabundance of size aggregates on the sheet surfaces. However, the self-assembled hydrophobic components made nearly no contribution to sizing enhancement and, conversely, brought about a sizing reduction. Thus, the aluminum components in the sized sheets have an inhibitory effect on hydrophobic size aggregation, and there must be an optimum demand for enhancing the sizing response. These results obtained in this study revealed that the additive balance controlling the size localization/delocalization characterized by the XPS/PyGC comparative analysis was one of the most striking factors in the sizing response.

CONCLUSIONS

The factors influencing sizing response in tub-sizing systems with an anionic emulsion size consisting of fatty acids were investigated with regard to the roles of aluminum components in sizing phenomena by XPS/PyGC comparative analysis. Size components in large quantities made nearly no contribution to the sizing appearance of alum-free sheets and hence size content did not reflect sizing features. The atomic ratio of carbon, indicating the surface abundance of size components on the sheet surfaces, was an excellent parameter for representing the sizing behaviour of tub-sized sheets. Eventually, aluminum components in the paper sheets must behave as an inhibitor for the undesirable aggregation of size particles and as a promoter for scattering the hydrophobic size components over the hydrophilic cellulose fibres, resulting in the enhancement of sizing effects.

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KEYWORDS: SIZED PAPERS, SURFACE PROPERTIES, ANIONIC COMPOUNDS, SIZE, FATTY ACIDS, ALUMINUM, SIZING EFFICIENCY.

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Mechanical Properties of Coating Layers

P. RÄTTÖ

The mechanical properties of coating layers containing a ground $CaCO_3$ pigment and a styrene– butadiene latex were modelled in terms of latex content and porosity. The pigment particles were assumed to be rigid, spherical and ordered in a face-centred cubic packing. The particles were assumed to be connected to each other by cylindrical latex bridges. Micromechanical modelling was used to calculate the stiffness of the coating layer. The calculations of the compressive stiffness using various coating formulations and porosities revealed that parameters other than latex content (porosity and microstructure) had an influence on the stiffness and strength of the coating layer. Increasing the latex content would increase the stiffness of the coating layer only as long as it is accompanied by a corresponding decrease in porosity.

Nous avons élaboré un modèle des propriétés mécaniques des sauces de couchage contenant du $CaCO_3$ en poudre et un latex de styrène-butadiène en nous fondant sur la teneur en latex et la porosité. Nous avons présumé que les particules de pigments étaient rigides, sphériques et organisées en un amas cubique à faces centrées, et qu'elles étaient reliées entre elles par des ponts de latex cylindriques. Nous avons utilisé la modélisation micromécanique pour calculer la rigidité de la couche. Les calculs de la rigidité compressive effectués à l'aide de diverses formulations et porosités de la sauce de couchage ont révélé que des paramètres autres que la teneur en latex (porosité et microstructure) avaient une influence sur la rigidité et la résistance de la couche. Augmenter la teneur en latex ne ferait qu'accroître la rigidité de la couche en autant si elle est accompagnée d'une diminution correspondante de la porosité.

INTRODUCTION

Most coated products are calendered to meet the demands for smoothness, gloss and printing performance. The smoother surface is a result of a more even thickness profile of the paper. At the same time, the bending stiffness and opacity of the paper are reduced as a result of the reduced thickness of the paper. Thus, the surface properties are improved at the expense of the mechanical and optical properties of the paper.

The coating layer consists of pigment particles bound together by latex in a porous network. Thus, the mechanical properties of the coating layer will depend of the cohesion of the latex bridges formed between the pigment particles, the adhesion between the latex and the pigment particles and the void structure of the coating layer. Generally, stiffer latices should give stiffer coating layers. However, stiffer latices will prevent shrinking during drying and consolidation and therefore give a more porous structure [1,2]. The more porous structure will be softer due to the ability to compact volumetrically under compression more than a denser structure. Since the pigment particles are usually stiffer than the latex bridges, most of the deformation can be considered to be due to the deformation of latex bridges. Then, a stiffer latex bridge would give a stiffer coating layer. However, a higher porosity of the coating layer would be enabled by larger interparticle distances, thus decreasing the stiffness of the coating layer.

Kan et al. [3] used dynamical mechanical spectroscopy to measure the viscoelastic properties of coating layers. The storage modulus of the coating layers depended on the latex content, the void volume and the type of latex. Increasing the volume concentration of latex increased the storage modulus of the coating layer below the glass transition temperature and decreased the stiffness of the coating layer above the glass transition temperature. The glass transition temperatures of the coating layers coincided with the glass transition temperatures of the latices. Kan used the Williams, Landel, Ferry equation to describe the time–temperature superposition of the viscoelastic properties of the coating layer.

The improvement in surface properties of uncoated paper depends on how the paper is compressed in the calender nip [4]. The results of Wikström et al. [5] indicated that the same applies for coated papers also. Wikström used platen press tests to study the out-of-plane compression properties of coating layers. Coating layers with various latices were compressed at 23 and 150°C. Wikström found that the out-of-plane compression properties of the coating layers were related to the mechanical properties of the latex.

To a great extent, the mechanical properties of the coating layer depend on the geometric arrangement of the pigment particles and of the latex bridges between the particles. Lepoutre and Rigdahl [6] used composite-material models to describe the influence of the geometric structure of pigment particles on the elastic modulus of the coating layers. Toivakka and Bousfield [7] used spherical particles within a random packing to describe the viscoelastic properties of coating layers. By raising the latex content, the radius of the cylindrical latex bridges increased and thus the stiffness of the coating layer increased. Prall et al. [8] measured the viscoelastic mechanical properties of pigmented coatings and found that the pigment shape and the pigment volume concentration were important parameters for the mechanical properties of coating layers.

In this work, the out-of-plane compression has been measured on cast coating layers. Experimental parameters were the composition of the coating layer, which varied by varying

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the type of latex, latex content and the influence of pressure, pulse time and pressing temperature. Only one type of pigment has been used in this work.

A micromechanical model is proposed. By assuming a face-centred cubic (FCC) packing of spherical particles, the mechanical properties were calculated from the porosity, the latex content and the mechanical properties of the latex.

METHODS AND MATERIALS

Materials

Preparation of Coating Layers

The coatings were prepared using a casting technique. A high solids content coating colour (70% solids) was prepared. The coating colour was then degassed for one hour in an ultrasonic bath; model 28X from NDI, Yucaipa, CA, USA. The high solids content coating colour was then casted on a polytetraflourethylene membrane filter, Flouropore 0.2 μm from Millipore, Carrigtwohill, Ireland. The coating colour was prevented from floating out by a plastic ring with a diameter of 40 mm. Casting was performed by placing the ring between two filters with an excess of the coating colour. Pressure was then applied on the two filters to avoid forming air bubbles during casting. The coatings were then left to dry under pressure for 24 h, and then left to dry freely for another 24 h. Wikström et al. [5] have used a similar method to prepare thick coatings. The coatings were subjected to a temperature of 55°C for 20 min.

The cast coatings were then milled to an even thickness (2–3 mm) using a high-speed rotating metal cutter. This was done to prevent the influence of thickness variations on the out-of-plane compression during testing [5]. The thicknesses of the cast coating layers were ~2–3 mm, measured using SCAN Standard P7:75 [9].

Composition of the Coatings

A ground calcium carbonate pigment, Hydrocarb C60 from Omya AG, Ottringen, Switzerland, was used. Two different styrene–butadiene latices from Dow Chemical Europe, Horgen, Switzerland, were used, denoted latex 23 and latex 55, referring to the glass transition temperature in °C of each latex. The latices were chosen to obtain coating layers with different porosities. An amount of 0.5 parts per hundred parts of pigment (pph) of carboxymethyl cellulose, Finnfix-10, Metsa Specialty Chemicals, Äänekoski, Finland, was added to the coating colour.

Coating colours were prepared with three different latex contents: 10, 14 and 18 pph. The coating colours were denoted according to the latex type and the latex content, e.g. the coating layer containing 10 pph of latex 23 was denoted 23:10.

Testing Procedure

The porosity, *P*, before pressing was calculated as:

$$P = \left(1 - \frac{V_{solid}}{V_{sample}}\right) \times 100\% \qquad (1)$$

where V_{sample} is the volume of the coating layer and V_{solid} is the solids volume. V_{sample} was calculated from the measured thickness and the diameter of the coating layers and V_{solid} was calculated from the composition of the coating and the densities of the pigment and the latex.

For the platen press experiments, equipment from MTS, Eden Prairie, MN, USA, was used. The compressive load was built up using a hydraulic cylinder, which enabled loads up to 40 kN. The platen press was equipped with separate heating elements, enabling plate temperatures up to 180°C. Load and displacement was recorded in an analogue/digital converter and therefore the stress and strain could be followed continuously throughout the entire experiment.

Platen press experiments were performed using a haversine (half sine) pressure pulse. The amplitude of the pressure pulse was 30 MPa. The pressure was applied with three different pulse times: 60, 600 and 6000 ms elapsed during the compressive stroke. The coatings containing latex 23 were compressed at 23°C and the coating colours containing latex 55 were compressed at four different temperatures, 23, 50, 75 and 85°C to study the influence of the glass transition temperature of the latex on the compressive behaviour of the coating layer. A pressing temperature at the glass transition temperature of the latices was chosen to compare the coating layers at similar aggregation states of the two latices, i.e. leathery. For each test point, two specimens were tested. To achieve an even temperature within the coating layer, the coatings were preheated before each test. Any temperature rise due to deformation energy has been neglected.

The thicknesses of the coatings were determined using the displacement transducer in the platen press equipment. The compressive strain, *ε*, is reported as the logarithm of the ratio of the thickness of the coating layer under compression, *d*, over its initial thickness, d_0 (before loading) [10]:

$$\varepsilon = \ln \frac{d}{d_0} \qquad (2)$$

The stiffness was evaluated as the secant modulus at 30 MPa. The secant modulus is defined as the stress divided by the strain:

$$E = \frac{\sigma}{\varepsilon} \qquad (3)$$

Compression, or thickness reduction, will give negative strains and pressure will give negative stresses. The strain levels in these experiments were between −0.7 and −13%.

RESULTS

Figure 1 shows the secant modulus at 30 MPa for all coating layers at pulse time 600 ms and temperature 23°C. The stiffness of the coating layer decreased with increasing pulse time (not shown here) as a result of the viscoelastic character of the materials. The two latices showed different behaviours. For the coating layers containing latex 23, the stiffness of the coating layer increased with the latex content. For the coating layers containing latex 55, no clear relationship between the secant modulus and the latex content could be observed. Note that the stiffness of the coating layers, ~1 GPa, was considerably higher than the compressive stiffness of paper in the thickness direction, i.e. ~0.05 GPa [11].

Figure 2 shows the secant modulus evaluated at 30 MPa of coatings 55:10 at the temperatures 23, 40, 55 and 80°C. The secant modulus of the coating layers decreased

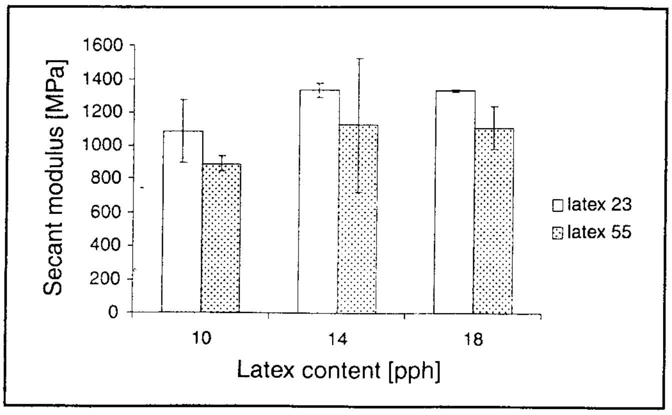

Fig. 1. The secant modulus for all coating layers at the pulse time 600 ms and temperature 23°C. The error bars indicate the 95% confidence limits.

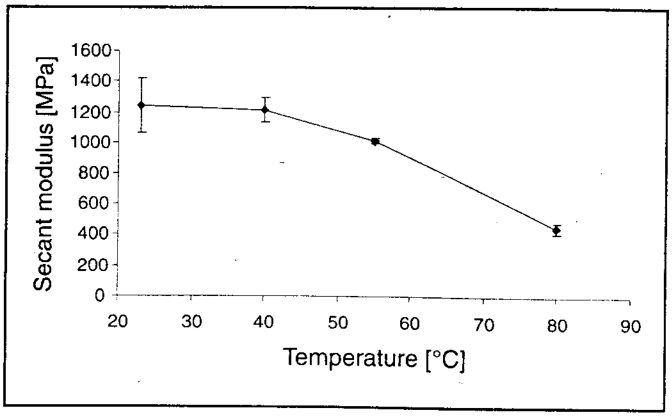

Fig. 2. The secant modulus evaluated at 30 MPa and pulse time 600 ms as a function of temperature for coating layers 55:10. The error bars indicate the 95% confidence limits.

significantly around the glass transition temperature of the latex, 55°C. At 80°C, the secant modulus decreased even further. At this temperature, the secant modulus at 30 MPa is no longer a relevant method to evaluate the stiffness of the coating layer, since 30 MPa is probably considerably higher than the yield strength of the material at this temperature. The material behaves like a viscoplastic solid rather than a viscoelastic one at this temperature. A more appropriate measurement of the stiffness would be the secant modulus at a lower stress level, below the yield strength of the material.

Figure 3 shows the secant modulus of coatings 55:10, 55:14 and 55:18 at 55°C. At this temperature, the latex is at its glass transition temperature. Generally, the stiffness was lower than that of the coatings containing latex 23 at its glass transition temperature. This was quite surprising, because latex 55 had a higher loss tangent at the glass transition temperature. However, some of this effect can be explained by the higher porosity of the coating layers containing latex 55 (Table I). The secant modulus of the coating layers containing latex 55 also showed a reversed trend with the latex content compared with latex 23: as the latex content increased, the secant modulus decreased. Since the opposite behaviour was noted for latex 23 at the glass transition temperature, this indicates that the latex content is not the only parameter influencing the stiffness of the coating layer, but that other factors, such as porosity and microstructure, influence the stiffness. At 80°C, not shown, the same effect could be seen but was more pronounced as a result of yielding and plastic flow.

MODELLING THE COMPRESSIVE BEHAVIOUR OF THE COATING LAYERS

Volume Model

The particles were assumed to be spherical, of the same radius and arranged in FCC packing (Fig. 4). It was further assumed that the latex had formed a film, resulting in latex bridges between the pigment particles. The latex bridges are assumed to be cylindrical and of the same radius and length. To calculate the particle distances and the radius of the latex bridges, a reference volume, V_{ref}, was used. As an example, the reference volume could be the volume of 1 kg of coating layer. In this reference volume, the pigment volume, the latex volume and the pore volume are considered. The densities of the coating layers are given in Table I. The mass fraction of the pigment and the latex content are given by the coating formulation. The density of the pigment is assumed to be 2700 kg/m^3 and the density of the latex is assumed to be 1020 kg/m^3. The mean particle radius, r_p, of the pigment was 0.3 μm.

The volume that the pigment particles occupy, V_p, in the reference volume can be calculated by dividing the mass of the pigment particles by the density of the pigment particles

$$V_p = \frac{m_p}{\rho_p} \tag{4}$$

where m_p is the mass of the pigment particles and ρ_p is the density of the particles.

Since the particle radius, r_p, was 0.3 μm, the number of particles, n, in the reference volume then can be calculated by dividing the particle volume by the volume of one particle

$$n = \frac{V_p}{\frac{4 \times \pi \times r_p^{\,3}}{3}} \tag{5}$$

The volume was calculated by letting the same number of particles grow inside the same volume, V_{ref}, until they reached contact. This would be at a particle size corresponding to a maximum particle radius, $r_{\max}$ (Fig. 4). The particle distance then can be calculated from the difference between the maximum particle radius, $r_{\max}$, and the actual particle radius, r_p.

The maximum packing ratio for spherical particles in an FCC cell is 0.74. The maximum volume that the particles can occupy, V_{max}, in the reference volume, V_{ref}, is therefore given by

$$V_{\max} = V_{ref} \times 0.74 \tag{6}$$

The maximum radius, r_{max}, of the same number of particles as calculated in Eq. (5) in the reference volume was then calculated as

$$r_{\max} = \sqrt[3]{\frac{3 \times V_{\max}}{4 \times \pi \times n}} \tag{7}$$

An illustration of the difference between the maximum radius, r_{max}, and the particle radius, r_p, is given in Fig. 4. The particle distance is defined as twice the difference in particle radius

$$d = 2 \times \left(r_{\max} - r_p\right) \tag{8}$$

and the side of the unit cell is

$$a = 2 \times r_{\max} \times \sqrt{2} \tag{9}$$

To calculate the radius of the latex bridge, the latex volume per particle is calculated

$$v_l = \frac{m_l}{\rho_l} \times \frac{1}{n} \tag{10}$$

where v_l is the volume of latex per particle, m_l is

TABLE I
THE DENSITY, POROSITY, MAXIMUM RADIUS ACCORDING TO EQ. (8), PARTICLE DISTANCE AND RADIUS OF THE LATEX BRIDGE

Coating	Density (kg/m³)	Porosity (%)	r_{max} (μm)	d (μm)	r_l (μm)
23:10	1774	24.5	0.322	0.0444	0.116
23:14	1816	19.2	0.324	0.0471	0.130
23:18	1848	14.4	0.325	0.0507	0.141
55:10	1727	26.5	0.325	0.0502	0.114
55:14	1679	25.2	0.332	0.0642	0.124
55:18	1626	24.7	0.340	0.0791	0.131

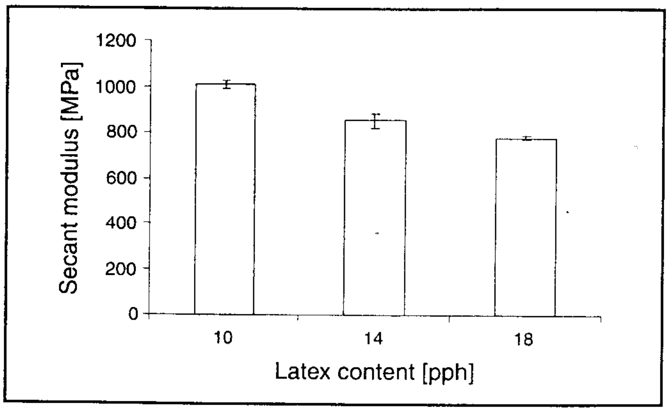

Fig. 3. The secant modulus evaluated at 30 MPa of the coating layers containing latex 55 at 55°C and pulse time 600 ms. The error bars indicate the 95% confidence limits.

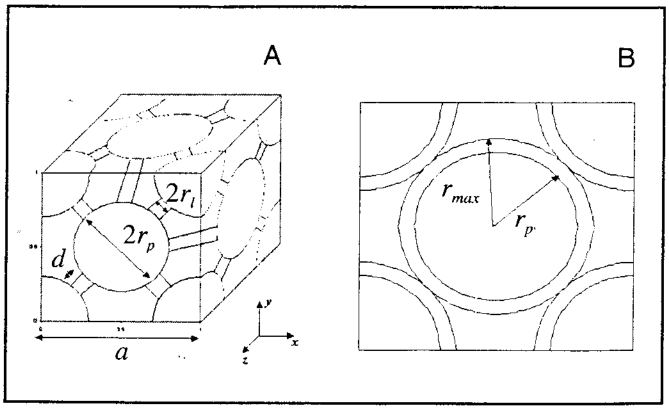

Fig. 4. Structure of the FCC unit cell (A) with some of the latex bridges marked out and (B) schematic illustration of the difference between the particle radius, r_p, and the maximum radius, r_{max}.

the mass of latex in the reference volume, and ρ_l is the density of the latex.

If it is assumed that the latex bridges are formed only between the closest particles, the number of latex bridges around each particle is 12.

The volume of each latex bridge is then given by

$$v_{bridge} = \frac{v_l}{12} \tag{11}$$

If the latex bridges are assumed to be in the shape of cylinders between the particles, the radius of each latex bridge can be obtained from the equation

$$v_{bridge} = \pi \times {r_l}^2 \times \frac{d}{2} + \pi \times {r_l}^2 \times \left(1 - \sqrt{1 - \frac{{r_l}^2}{{r_p}^2}}\right) - \frac{1}{3}\pi \times h^2 \times \left(3 \times {r_l}^2 - \left(1 - \sqrt{1 - \frac{{r_l}^2}{{r_p}^2}}\right)\right) \tag{12}$$

where r_l is the radius of the cylindrical latex bridge and h is given in Fig. 5. Half the interparticle distance is chosen, since each bridge is shared by two particles.

The particle distances in the unit cell, the radius of the latex bridge and the dimensions of the unit cells of the various coating layers are given in Table I.

Deformation of the Unit Cell

Deformation of the unit cell can be achieved through compression/tension of the latex bridges, shear over the latex bridge and rotation of particles giving a bending moment over the latex bridges. The bending moment of the latex bridges is assumed to be negligible because of the high ratio between the radius of the latex bridge and the particle distance ($r_l/d > 1.5$). It is assumed further that deformation of the unit cell will only take place in the y direction and that no deformation of the unit cell is obtained in the x or z directions.

The displacement in the y direction is denoted as u. Note that u is a negative value for compression. The new height of the unit cell is then given by $a' = a + u$. The strain of the unit cell in the y direction can be expressed as

$$\varepsilon = \ln\left(\frac{a'}{a}\right) = \ln\left(\frac{a+u}{a}\right) \tag{13}$$

In further analysis, one eighth of the unit cell is used, and the result can be transferred to the rest of the unit cell due to symmetry. The part of the unit cell and the latex bridge described in the analysis are marked in Fig. 5.

At the displacement of $u = 0$, the latex bridge will have angle of –45° to the x axis. When a displacement is imposed on the unit cell, the latex bridge will both distort and change length, resulting in both shear and compressive strains (Fig. 6). The starting point of the latex bridge in the x–y coordinate system is

$$(x_1, y_1) = \left(\frac{r_p}{\sqrt{2}}, a' - \frac{r_p}{\sqrt{2}}\right) \tag{14}$$

and the end point of the latex bridge is

$$(x_2, y_2) = \left(\frac{a}{2} - \frac{r_p}{\sqrt{2}}, \frac{a'}{2} + \frac{r_p}{\sqrt{2}}\right) \tag{15}$$

The length of the latex bridge in the deformed unit cell is given by

$$d' = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2} \tag{16}$$

and the angle of the latex bridge by

$$\theta = \arctan\left(\frac{y_2 - y_1}{x_2 - x_1}\right) \tag{17}$$

The strain of the latex bridge is then

$$\varepsilon' = \ln\left(\frac{d'}{d}\right) \tag{18}$$

The resulting forces in the global x–y coordinate system can be calculated using Hooke's law

$$F_x^\varepsilon = \frac{\pi}{2} \times {r_l}^2 \times E_{latex} \times \varepsilon' \cos\theta$$

$$F_y^\varepsilon = \frac{\pi}{2} \times {r_l}^2 \times E_{latex} \times \varepsilon' \sin\theta \tag{19}$$

where E_{latex} is the elastic modulus of the latex. The force has been divided by two since only half the latex bridge is inside the volume considered, one eighth of the unit cell.

The shear deformation of the latex bridge can be calculated from the difference in angle (Fig. 6)

$$\gamma = -\frac{\pi}{4} - \theta \tag{20}$$

The resulting forces in the x–y coordinate system due to the shear of the latex bridge can be calculated

$$F_x^\gamma = -\frac{\pi}{2} \times {r_l}^2 \times G_{latex} \times \gamma \times \sin\theta$$

$$F_y^\gamma = -\frac{\pi}{2} \times {r_l}^2 \times G_{latex} \times \gamma \times \cos\theta \tag{21}$$

where G_{latex} is the shear modulus of the latex. The force has been divided by two since only half the latex bridge is inside the volume considered, one eighth of the unit cell.

If it is assumed that the force on the top of the unit cell is P, then the force on the cube is $P/4$. Since the other stresses for latex bridges in the volume considered result in the same forces, the total stresses from the latex bridge is multiplied by 4. The force can be calculated from the equilibrium of forces in the y direction

$$\frac{P}{4} = 4 \times (F_y^\varepsilon + F_y^\gamma) \tag{22}$$

The secant modulus of the unit cell can then be calculated from:

$$E = \frac{\sigma}{\varepsilon} = \frac{\left(\frac{16 \times (F_y^\varepsilon + F_y^\gamma)}{a^2}\right)}{\varepsilon} \tag{23}$$

Figure 7 shows the calculated stiffnesses for six different coating layers. The porosities were taken from the coating layers used in the trials. The elastic modulus of the latex was assumed to be 400 MPa and the shear modulus of the latex was assumed to be 154 MPa. The values were chosen by trial and error to fit the experimental data, but are in the same range of magnitude as used by Lepoutre and Rigdahl [6] (~200 MPa for styrene–butadiene latex at its glass transition temperature). The strain applied on the coating layers was –0.005. The porosities

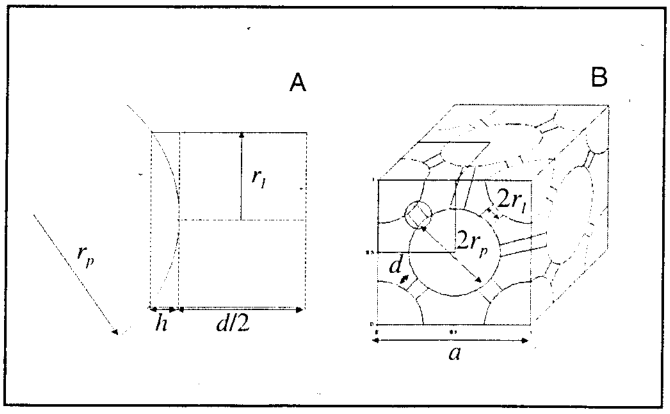

Fig. 5. Schematic illustration of (A) half a latex bridge and (B) the marking of eight of the unit cells used in the analysis.

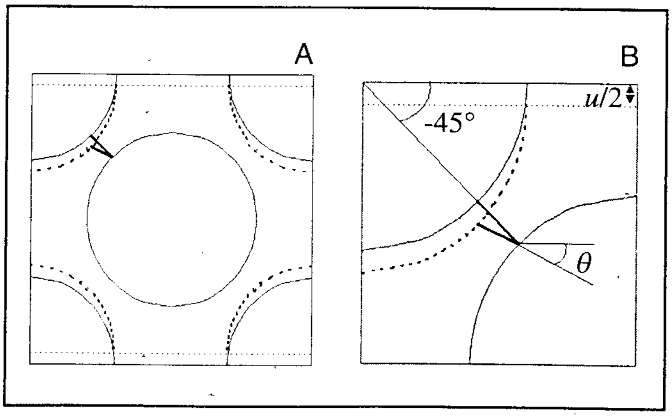

Fig. 6. Schematic illustration of the deformation of the unit cell with the displacement u. (A) The whole unit cell and (B) the deformation of the latex bridge.

corresponding to latex 23 gave an increasing stiffness with the latex content while, with latex 55, the porosities decreased with increasing latex content. This illustrates the importance of the geometric arrangment of the pigment particles and the latex bridges on the mechanical properties of the coating layer.

Comparison with Experimental Data

To compare experimental data with the calculated data, the secant modulus at the glass transition temperature of the latex was used. The two latices are not expected to behave exactly in the same manner at the glass transition temperature, since the loss tangents or the damping factors are quite different. However, the comparison gave an indication of the influence of the geometric structure on the stiffness of the coating layer.

Figure 8 shows the measured stiffness against the calculated stiffness of the coating layers at the glass transition temperature for each latex. The calculated values correlated well with the experimental data despite the simplicity of the model. It should be kept in mind that the material data for the latices, E modulus of 400 MPa and shear modulus of 154 MPa, were chosen to produce good correlation with the experimental data. However, the influence of the porosity and latex content on the mechanical properties was well described by the model for the various coating formulations.

DISCUSSION

The coating layers containing latex 23 and latex 55 behaved quite differently as a function of latex content. Most of this can be explained by the difference in porosity, which is the result of geometric effects at the microstructural level of the coating layer. It might be appropriate to add a few comments regarding the experimental data on stiffness. At 23°C, the patterns were quite clear for coatings containing latex 23; the stiffness increased with the latex content, while no clear patterns could be seen for coatings containing latex 55 regarding the stiffness at 23°C. As the temperature increased to the glass transition temperatures of latex 55, the patterns started to become more significant. Some of this can be attributed to the glassy state of latex 55 at 23°C, which makes it harder to produce relevant test data in compression.

The mechanical properties of coatings are affected greatly by the mechanical properties of the binder. In this work, two latex binders had been used and the effect of the latex content on the mechanical properties of the coating differed for the two latices. Latex 23, with a low glass transition temperature, behaved as expected, that is, the stiffness of the coating layer increased with increasing latex content. Latex 55, with a high glass transition temperature, showed the opposite effect. To some extent, this can be explained by the geometric structure of the coating layer. The stiffness of the coating layer depends on both the interparticle distance and the diameter of the latex bridges. Both parameters depend on the porosity of the coating layer which, in turn, depends on the stiffness of the binder at the drying temperature [1,2,6].

The model illustrates the importance of including porosity when predicting the effect of latex content on the mechanical properties of the coating layer. Apart from the mechanical properties of the latex, the stiffness of the material depends both on the diameter of the latex bridges and their length. If packing is looser, which is much more realistic, then the interparticle distance between neighbouring particles would be longer, the number of neighbouring particles would be smaller and the geometry of the cylindrical latex bridges would be different. With regard to packing, if packing is looser than FCC, which is more realistic, it seems plausible that the longer interparticle distance between the particles would give a less stiff material than with the FCC packing.

The model certainly can be improved in a number of ways:

— Out-of-plane displacements in the x and y directions have been neglected. This was done to simplify the calculations. To describe the deformation of other pigment systems, it would also be necessary to build up a different unit cell.

— When modelling the coating layer, one important factor is the mechanical properties of the binder. In this work, a linear elastic material model has been used for the latex. The mechanical properties of latices can be nonlinear and indefinitely viscoelastic/viscoplastic. The model can be improved further with a better material model for the latex, which would also include yielding. It would then be possible to describe the effect of calendering on the deformation and, thus, porosity of the coating layer. The latter would be of great importance for the printing properties of the paper product. It shall be emphasized, in this case, that the coating layer is considerably stiffer than the paper and that even small deformations of the coating layer might have a great influence on the porosity.

— To model yielding of the coating layer, particle motion and particle sliding would have to be included in the description. In this case, also, the shear strength of the latex will be of great importance for the mechanical properties of the coating layer.

CONCLUSIONS

The model presented in this paper involves some simplifications. The pigment particles are not likely to be ordered in an FCC packing, but are more likely to be arranged randomly. A different packing structure will probably influence the calculated results significantly. The ground $CaCO_3$ particles are not perfectly spherical, either, and this might influence the results of the model further. However, the model does describe the influence of the mean particle distance in the coating layer on the mechanical properties, which was the aim of the work presented here, and it does so quite well despite its simplicity.

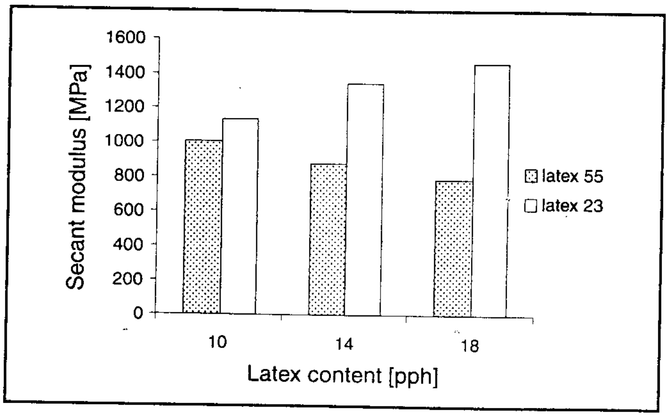

Fig. 7. The calculated secant modulus of the coating layers. The calculated data were obtained assuming an elastic modulus of 400 MPa and a shear modulus of 154 MPa.

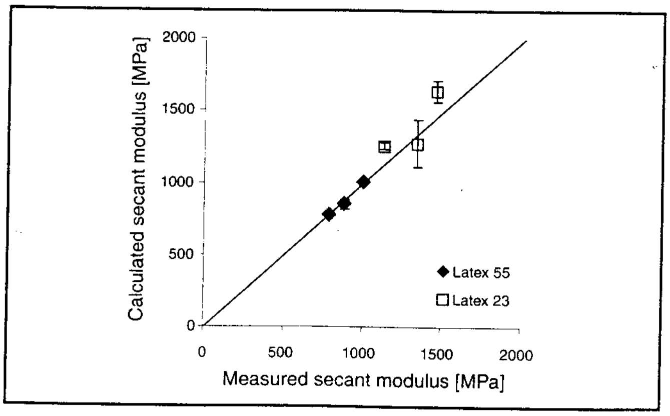

Fig. 8. The measured secant modulus of the coating layer at 30 MPa and a pulse time of 600 ms versus the calculated secant modulus. The temperature was 23°C for latex 23 and 55°C for latex 55, which is equivalent to the glass transition temperatures of the latices. The calculated data were obtained assuming an elastic modulus of 400 MPa and a shear modulus of 154 MPa. The error bars indicate the 95% confidence limits.

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KEYWORDS: COATINGS, LAYERS, MECHANICAL PROPERTIES, CALCIUM CARBONATE, STYRENE, BUTADIENE, LATEX, MODELS, PIGMENTS, PARTICLES, POROSITY.

An investigation of latex particle clustering in the wet coating color

RONALD L. VAN GILDER

ABSTRACT: Nonuniformity in the dispersion of the latex with the pigment was present in the wet coating color. The nonuniformity consisted of latex particles that clustered together and did not disperse well with the clay and calcium carbonate particles. Correspondingly, there was a nonuniform distribution of the latex with the pigment throughout the dried coating structure. Upon printing this nonuniform latex-pigment coating on a commercial 6-color sheet-fed press, a high degree of nonuniformity in the form of back-trap mottle (BTM) resulted.

In this paper, an investigation of the nonuniform dispersion of the latex and the pigment in the coating will be described and a mechanism for the latex particle clustering phenomenon will be presented.

Application: The dispersion uniformity of the latex and pigment in the wet coating color can influence the degree of uniformity in the dry paper coating and correspondingly, in the commercial print.

Earlier work attributes nonuniformity in the coating structure to binder migration[1] or the coalescence of latex binders to different degrees during drying [1a]. Binder migration generally has occurred when using an inappropriate drying strategy. Engstom and Rigdahl conducted an extensive literature review of the work on binder migration and the subsequent effect on printability and print quality [1]. More recently, work by Kim-Habermehl et al [2] showed how to optimize the drying process for paper coatings, specifically for reducing print variations such as back-trap mottle. From previous work, we also know that latex binders with higher film formation temperatures coalesce to different degrees during drying [1a].

The latexes used in this work, however, had relatively low film formation temperatures, and would not be expected to result in varying degrees of coalescence under different drying conditions. Similarly, the propensity for binder migration should be relatively low.

What is new in this paper is that nonuniformity of the wet coating color consisted of latex particle clusters that did not disperse well with the inorganic pigments. We also observed this nonuniform distribution of the latex with the pigment in the dry coating structure. Furthermore, upon printing, the nonuniform latex coating resulted in a high level of back-trap mottle (BTM) in a commercial 6-color sheet-fed press evaluation. This new source of nonuniformity, which has been observed in a number of different cases, is described in this paper.

THEORETICAL CONSIDERATIONS

Previous work has shown that the latex binder concentrated in different locations of the coating thickness through binder migration [7]. In this work, however, there was a lack of dispersion uniformity of the latex and pigment throughout the coating layer. Different structures have been proposed, theoretically, for latex particles when brought into contact with the mineral pigments [3] and how these latex particles are dispersed. One proposal for a coating structure consisted of latex particles that are well dispersed on the surface of the pigments and that during drying may spread and form a very thin continuous latex polymeric film on the pigments. Another proposal suggests that the latex particles may form aggregates consisting of many particles. In the latter case, packets of polymer particles—commonly referred to as spot-welds— would bind the pigment particles. The authors of that work speculated that such particle aggregation could be induced by the different water-soluble polymers in the liquid phase of the coating. Different interactions between the latex and pigment could occur along with possibly a redistribution of adsorbed material on the pigment or latex polymer particle surfaces. This work will lend some support to those two coating structure proposals.

A common assumption is that latex particles will uniformly disperse with the pigment particles when a wet latex coating color is prepared. This is understandable because there are few published reports on the lack of latex dispersion uniformity in the wet coating color.

Whalen-Shaw and Sheehan [4] used cryo-scanning electron microscopy (cryo-SEM) to visualize the different coating color components of the wet coating. This work focused on wet microstructures resulting from component interactions involving the following:

A. Latex with carboxymethyl cellulose
B. Styrene-butadiene latex-water suspensions
C. A protein styrene-butadiene latex interpolymer with clay.

The analyses of these microstructures were made at relatively low solids. In the case of the standard nonreactive latex A, using a 5% w/w (weight—on-wet) concentration, monomodal spheres were observed. Latex B (a pH sensitive latex with capability to associate with clay)—again under a dilute concentration of 5% w/w—showed clusters of spheres. Such clustering of the latex particles with this particular latex was not seen when an inorganic pigment was present at the higher application solids level.

Our work, in contrast, did investigate the effect of latex type on the clustering phenomenon, in the presence of the inorganic pigment in the wet coating color, at the relatively high solids level of application. In addition, the study used cryogenic transmission electron microscopy (cryo-TEM) instead of cryo-SEM to achieve a higher resolution of the components and provide the required detail to gain a greater understanding of the wet coating color dispersion uniformity.

Davis [5] used a theory of competition between particle aggregation and particle breakup at different shear rates to describe the colloidal forces that determine the structure of wet coating colors. In our work, however, the latex clustering phenomenon in the coating color did not appear to be affected over a relatively wide range of shear rates, so that such a theory was not used to explain our results. Instead, using microcalorimetric data and principles of thermodynamics, we propose a mechanism for the different degrees of latex clustering present in this work.

EXPERIMENTAL

Latex preparation and characterization

The latexes used in this work were prepared using the emulsion polymerization technique, but with different process conditions. Particle size was determined using a Brice-Phoenix photometer. The film formation temperature was determined on a minimum film formation temperature (MFFT) apparatus.

Micro-calorimetry of latex and pigment interactions

The heat of interaction between the different latexes and the pigments was determined using the isothermal titration calorimeter (ITC) and the procedure as described in previous work [6].

Pilot coater coatings

The coating formulation used in the pilot coater trial consisted of 75 parts of No.1 clay, 25 parts of fine ground calcium carbonate, 16 parts latex, 0.75 parts calcium stearate, and 0.5 parts of carboxymethyl cellulose. The solids level was 65% and the pH was 8.5. It should be mentioned that an optimum level of the sodium polyacrylate dispersant (0.1 parts) was used for the pigments in the wet coating color preparation, based upon the minimum viscosity in the dispersant demand curve (Brookfield viscosity vs. dispersant level).

For the cryogenic fixation of each of the coating colors, the coating colors were prepared under comparable mixing conditions (agitation rates and times) of the pilot coater coating preparation equipment, so that this would not be considered a factor in the results.

The coatings were applied at 18 g/m^2 coat weight per side to a surface-sized, wood-free base sheet using a flooded-nip blade applicator at a speed of 610 m/min. We used the same drying conditions for the two different coatings, consisting of a hard late drying configuration on the air flotation dryer units, but no infrared heating. The air set-point temperatures were 66°C, 66°C, 177°C, and 204°C respectively for the four air flotation dryer units.

The coated paper was supercalendered a total of four nips at a speed of 300 m/min and a pressure of 315 kN/m using a steel roll temperature of 93°C.

Cryogenic fixation and transmission electron microscopy (TEM) analysis of the wet coating colors

The different wet coating color samples from the pilot coater were quick-frozen by placing a small drop of the formulation on the tip of an aluminum cryo-sample pin, which was then plunged into liquid propane using a cryogenic fixation device. We sectioned the samples using a cryo-attachment equipped with a diamond knife. The thin sections were obtained at -120°C. The sections were transferred to a cryo-transfer holder and placed into the microscope using the standard port. The holder was warmed to -90°C and held at this temperature for approximately 5 min to freeze-dry the sections. The samples were then cooled to a temperature of -145°C for examination in the TEM, operating at an accelerating voltage of 120keV. Images were recorded at 9000 and 30,000 negative magnification using a slow scan camera.

Scanning electron microscopy (SEM) imaging of the coated paper surfaces

For the surface SEM analysis [7], we mounted the samples onto an aluminum SEM stub and coated them with a thin layer of conductive and contrast enhancing chromium. The samples were examined in the secondary imaging mode with a field emission gun SEM operating at a beam accelerating potential of 5 keV. Representative images were collected using a digital acquisition system and associated software.

Uniformity of ink oil absorption

N. Plowman Associates carried out the uniformity of ink oil absorption, according to their test procedure [8]. In this test, a fast-setting, low-tack gloss overprint offset varnish was printed from the blanket of the NPA laboratory press onto the paper. After a 7-second delay, a controlled film thickness of a high-tack, quick-set offset cyan ink was transferred from the blanket to the varnish layer. The result yielded a print that could be rated visually for the degree of uniformity. Using the system, a rating of "1" is good, declining to a rating of "5," which is bad.

Commercial 6-color sheet-fed print trial

A commercial 6-color sheet-offset press was used to evaluate the printing performance of the different coated papers in this work. We ran the press with a color sequence of black, cyan, magenta, yellow, black, and cyan. The press was run at a slower speed (5800 impressions per hour) than normal to accentuate back-trap mottle. The uniformity of the second down cyan was compared to that of the sixth down cyan to detect BTM. BTM was rated visually and measured on the Tobias meter.

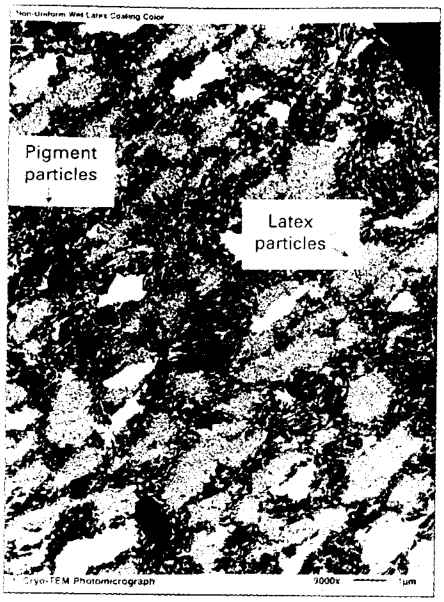
RESULTS AND DISCUSSION

The purpose of our work in this paper was to investigate the degree of nonuniformity in the wet latex coating colors and how this affected the dry coating structures and the commercial printing performance. In addition, an understanding of the latex clustering phenomenon was pursued.

Both the nonuniform and uniform latex coatings that were investigated in this work consisted of latexes that were comparable in particle-size (1500 A versus 1450 A respectively) as well as in carboxylation for stability so that binder migration could be minimized [1]. Both latexes had a relatively low minimum film formation temperature (MFFT =13°C versus 15°C respectively) so that there would be less tendency for nonuniformity in the coating structure resulting from dryer sensitivity [3].

Before discussing the results, note that for the coatings in this work, there was sufficient coating hold-out and fiber coverage and as a result these factors were not considered important in the nonuniformity observed.

The discussion of the results is organized in the following order:



1. Nonuniform latex wet coating color at the lower magnification of 9000x.

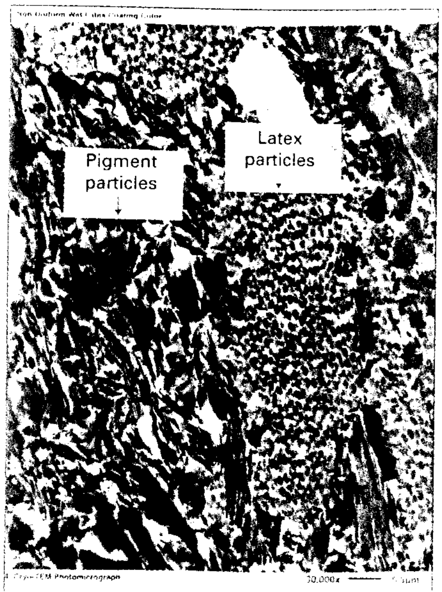
1. Wet coating color dispersion uniformity analysis using cryogenic fixation and transmission electron microscopy, TEM
2. Scanning electron microscopy (SEM) surface analysis
3. Uniformity of ink oil absorption
4. Commercial sheet-offset press BTM evaluation
5. Mechanistic aspects of latex particle clustering.

Wet coating color dispersion uniformity analysis using cryogenic fixation and cryo-TEM

Previous work has used high magnification cryo-SEM of wet coating microstructures to visualize directly components in both the diluted and concentrated coatings and to reveal component interactions [4]. Wet microstructures were examined in dispersions of clay, protein interpolymer S/B latex with clay, and S/B latex with carboxymethyl cellulose (CMC), as mentioned previously.

Based upon this earlier work and the advancements made in the cryo-fixation and cryo-TEM analysis [9-11], it was decided to investigate the degree of uniformity of the different wet coating color micro-structures using the cryo-TEM technique.

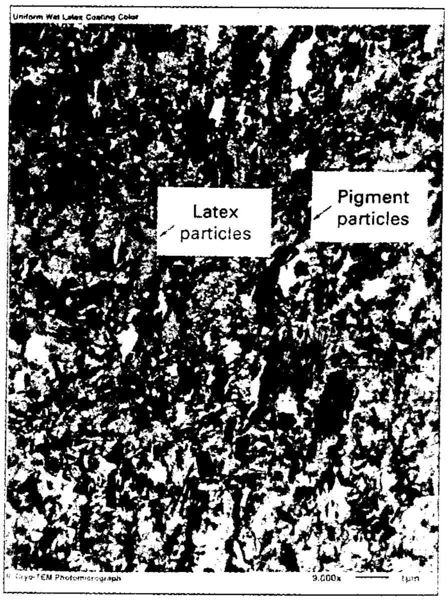
The cryogenic fixation procedure, as described above, fixes the microstructures of the original wet coating color in place without major disruptions in the structure. The main enabling principle, as discovered by Brueggler and Mayer [12], is that the water in the wet coating color changes into a vitreous or glass-like state when a cryogen such as liquid propane is used to provide a very rapid cooling rate. Extensive work on aqueous systems followed by Echlin [9] and others. The cooling rate of liquid propane is 10-12x10^3K/s versus 0.5x10^3K/s for liquid nitrogen. It is this vitreous state of water that locks or fixes the components of the coating color in place. After cryo-sectioning and freeze-drying, the individual particles of latex and pigment were observed in detail using TEM. The TEM analysis of the two wet coating colors revealed significant differences in how the latex particles were dispersed with the mineral pigment particles.



2. Latex particles at magnification of 30,000x.

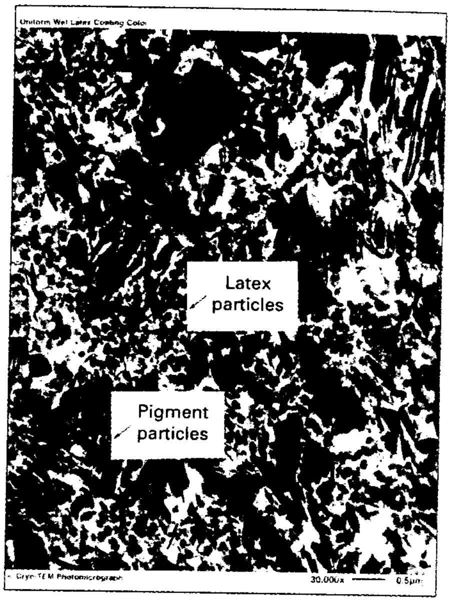
In the case of the nonuniform latex wet coating color, the cryo-TEMs showed that the latex particles did not disperse well with the mineral (clay and the calcium carbonate) pigment particles. Relatively large clusters of latex particles occurred frequently in the wet coating color. These latex particle clusters were segregated from the pigment particles, as shown for the nonuniform latex wet coating color in **Fig. 1** (cryo-TEM photomicrograph 1.) at the lower magnification of 9000x. These clustered latex particles did not intermingle with the mineral pigment particles and lacked dispersability with the pigment. This is very clearly shown at the higher magnification of 30,000x in **Figs. 2** and **3** (cryo-TEM photomicrographs 4 and 5.) where the latex particles have associated with themselves but not with the mineral pigment particles. This latex clustering phenomenon remained even when additional sodium polyacrylate dispersant (up to a 2.0 part level) was used in the coating color.

3. At 30,000x, it is evident that the latex particles have not associated with the mineral pigment particles.

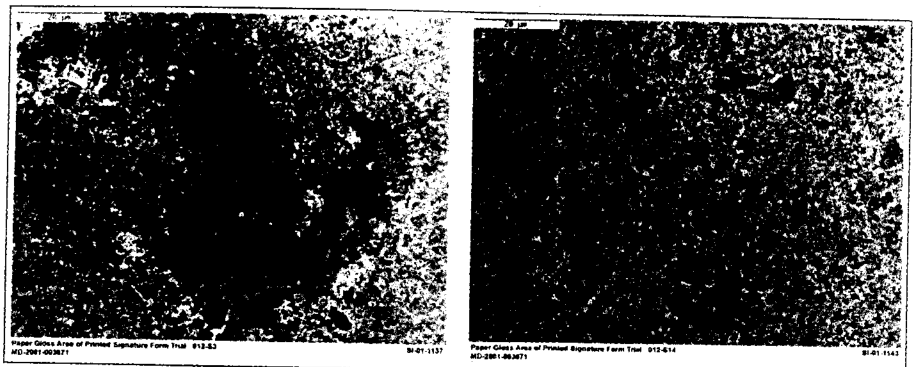


4. Uniform latex wet coating color, at 9000x magnification.

In an attempt to break apart these latex particle clusters, the coating color was mixed for an additional time with



5. Uniform latex wet coating color, at 30,000x magnification.



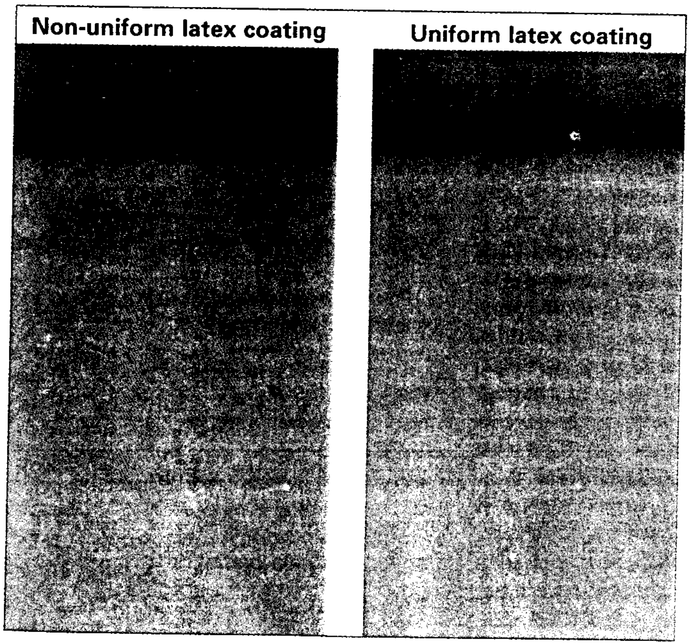
6. SEM 012-S3 (left) and SEM 012-S14 (right).

higher shear rates, but latex particles remained in distinct clusters. In contrast, in the case of the uniform latex wet coating color, the small spherical latex particles intermingled to a much greater extent with the mineral pigment particles (**Fig. 4**, cryo-TEM photomicrograph No.6, at 9000x magnification) and tended not to cluster to the extent of that in the nonuniform wet latex coating color. The higher magnification of 30,000x revealed a relatively uniform dispersion of the latex with the pigment (**Fig. 5**, cryo-TEM photomicrograph No.9).

SEM analysis of the coater paper surfaces

The SEMs of the coating surface for the nonuniform latex coating showed very distinct patches of sealed-off carbon-rich areas that were present next to the microporous coating structure (SEM 012-S3) (**Fig. 6**). The carbon-rich areas that were significantly darker than the microporous areas were attributed to the latex binder.

For the uniform latex coating, however, the SEM analysis revealed that the coating structure at the surface was relatively uniform and microporous without the larger sealed-off carbon-rich areas (SEM 012-S14) (Fig. 6). As a result, the nonuniformity of the nonuniform latex coating in the wet coating color was also seen in the dry coating structure.



7. Photograph of the uniformity of ink oil absorption (NPA test) prints, regular cyan (16 tack) over regular varnish-7 second delay.

Uniformity of ink oil absorption

In order to determine the effect of the nonuniform latex coating on the uniformity of ink oil absorption, testing was carried out by N. Plowman Associates, using the method as described above. The amount of trap of the cyan is dependent on both the change in tack of the varnish as well as the uniformity of that tack change. The uniformity of tack change can be a result of the degree of uniformity in the coating structure. The results of this test are used together with the results of the Paper and Ink Stability test to provide a prediction of mottle [8]. Mottle will occur most likely when there is nonuniformity present in the coating structure and the rate of ink-tack build or slope is relatively high.

Before carrying out the test, we knew from the ink stability test data that the nonuniform latex coating had a significantly higher slope (slope = 26.8) than that of the uniform latex coating (slope = 15.0).

When the ink oil absorption testing was carried out, the nonuniform latex coating showed significantly more mottle whereas the uniform latex coating showed a greater uniformity of the print, as shown in **Fig. 7** (photograph of the uniformity of ink oil absorption [NPA test] prints.) Even when a slower setting varnish was used to trap the cyan ink, there was still severe mottle present in the nonuniform latex coating. In other words, these results indicated that the nonuniformity in the coating could not be overcome in a commercial sheet-fed press by printing with a slower-setting ink.

Commercial 6-color sheet-offset press trial evaluation of the coated papers

The commercial six-color sheet-offset press was run with tack rated quick-set inks arranged in the proper sequence so wet-trapping mottle was not a concern. The color sequence from the first through the sixth station was black, cyan, magenta, yellow, black, and cyan.

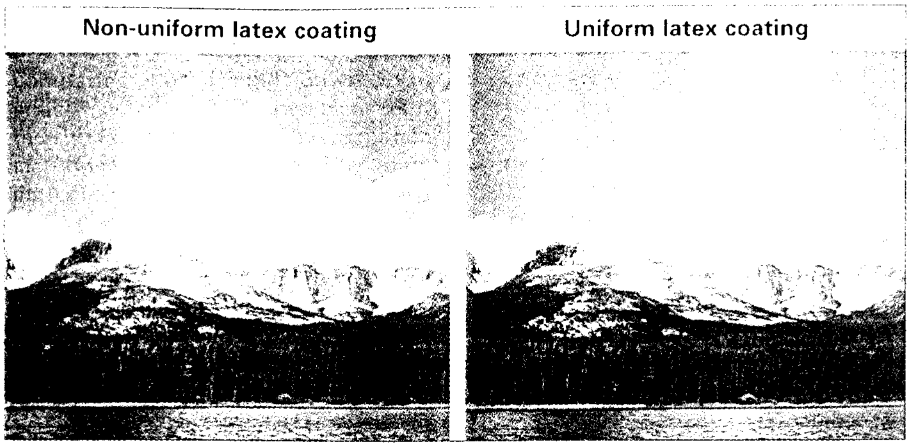
The extent of back-trap mottle in the print signature was established by comparing the second down cyan, which contacted four more blankets to the sixth down cyan, which did not contact any additional blankets. The uniformity of the second down vs. sixth down cyan was rated visually and was also measured on the Tobias meter. In addition, the sky in the photograph was rated visually for the degree of mottle.

Three criteria must exist for BTM to occur on press [8a]:

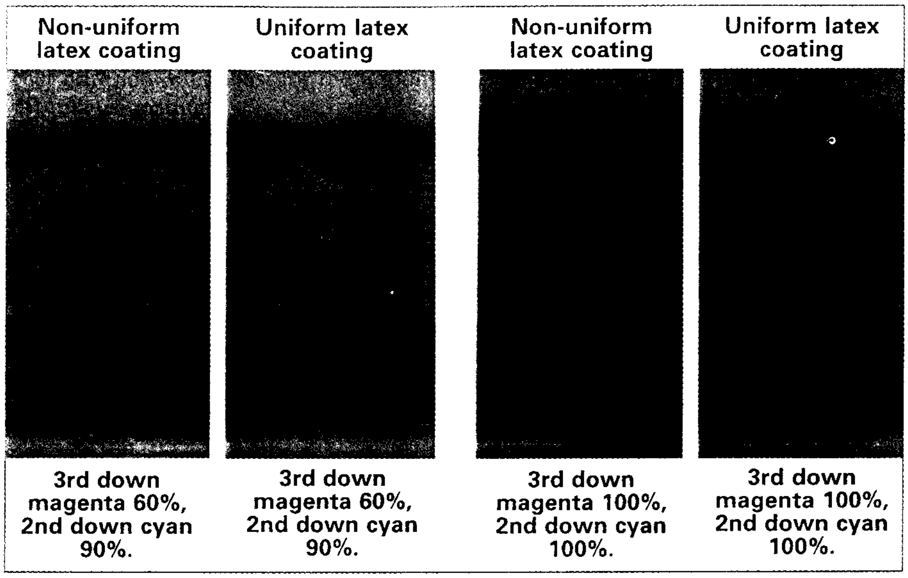
1. A fast setting ink
2. A fast ink-setting paper
3. A nonuniform coating on the paper.

In the commercial 6-color sheet-fed press evaluation, criteria 1 and 2 did exist. As stated above, it was determined that criterion 3 did exist for the nonuniform latex coating.

From the print signature of the nonuniform latex coating, it was observed that the sky in the photograph was very mottled in appearance whereas the sky in the uniform latex coating print was more uniform (**Fig. 8**, photograph in the commercial 6-color sheet-fed press print signatures). The mottled appearance can also be seen in **Fig. 9** for the trapping of the third down magenta over the second down cyan for the nonuniform coating as compared to that of the uniform coating. For the nonuniform coating, the second down cyan was very highly mottled, with a visual rating of 5 (1=best; 5= worst) and a Tobias reading of 1000 (the higher the number, the greater the mottle). In contrast, the sixth down cyan was very uniform, with a visual rating of 1 and a Tobias reading of 230, as shown in **Fig. 10** (photograph of back-trap mottle in commercial 6-color sheet-fed press.). Because the second down cyan was highly mottled, but not the sixth down cyan, this condition was described as back-trap mottle (BTM). The print signature of the uniform latex coating showed a very uniform second down cyan (visual rating of 1 and a Tobias reading of 300) and this was comparable to that of the sixth down cyan (visual rating of 1 and a Tobias reading of 250).



8. Photograph in the commercial 6-color sheet-fed press print signatures. Note mottled appearance.



9. Photograph of back-trap mottle in commercial 6-color sheet-fed press.

MECHANISTIC ASPECTS OF LATEX CLUSTERING

From the above discussion for the nonuniform latex coating, we speculate that, from the aggregation of latex particles into clusters, these clusters could then amalgamate into larger masses during the application and consolidation of the coating until the structure was immobilized. Upon drying, these larger masses would result in patches or an irregular distribution of latex film with the pigment particles. Such an irregular or nonuniform distribution of latex throughout the coating structure would result in different ink setting rates for the sealed-off latex film patches versus the microporous coating areas. As a result, nonuniformity during printing in the form of back-trap mottle would occur.

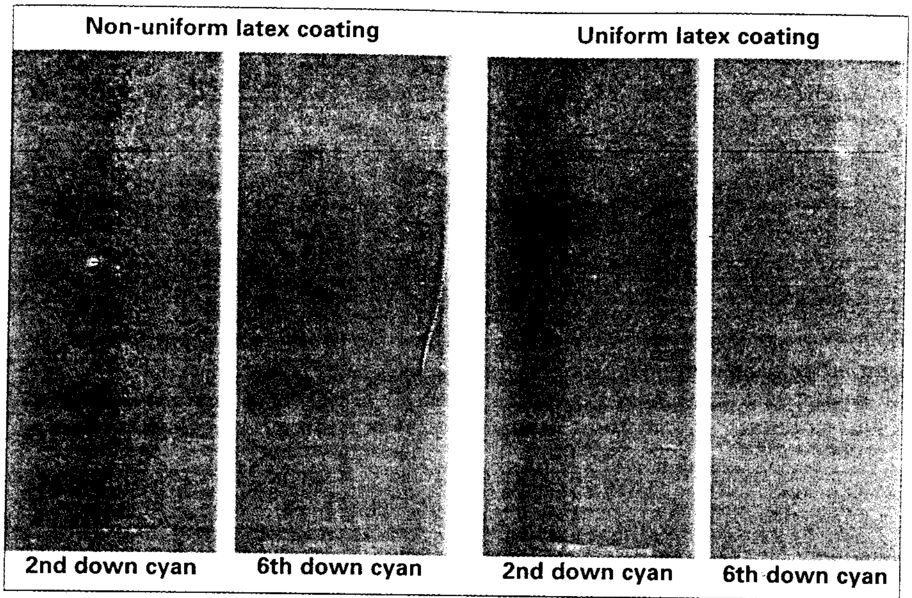
To provide one of the possible explanations for the differences in the degree of latex clustering observed in this work, the following discussion relates to thermodynamic principles. As mentioned above, it was not possible to explain the clustering phenomenon based upon the general latex polymer properties, such as particle-size and minimum film formation temperature, which were similar for the different latexes used in this work.

This work indicates that the differences in the degree of latex particle clustering was controlled by enthalpy and entropy effects of the coating colors in order to obtain a thermodynamically favored free energy state.

From a thermodynamic view, for the two different latex coatings, the following general relationship [13] could be used:

Delta G = Delta H - T x Delta S

where Delta G = free energy, Delta H = enthalpy, Delta S = entropy, and T = temperature.


Non-uniform latex coating

Uniform latex coating

2nd down cyan

6th down cyan

2nd down cyan

6th down cyan

10. Photograph of back-trap mottle in commercial 6-color sheet-fed press.

It is a favored thermodynamic condition when the free energy term, Delta G, is negative or minimized. This can be a result of either the enthalpy or the entropy effect or a combination of both. An increase in the delta entropy term is also thermodynamically favored.

To continue this investigation, we decided to do some further work, first based upon the enthalpy term of the thermodynamic relationship above. Microcalorimetry, as described in earlier work [6], was used to detect the enthalpy differences, either exothermic or endothermic, which resulted from the interaction of the different latices with the pigments in the wet coating colors.

As in previous work, it was possible to determine the enthalpy effects of the four basic interactions:

a. Latex surface-pigment surface
b. Latex surface-pigment supernatant
c. Latex serum-pigment surface
d. Latex serum-pigment supernatant.

However, in this work, only the following interactions showed relevant differences between the uniform versus nonuniform wet latex coating colors respectively:

b. Latex surface-pigment supernatant
   (-2384 vs. +153 microcalories)
c. Latex serum-pigment surface
   (-944 vs. -441 microcalories).

This data showed that, for the uniform latex coating, there was a strong latex particle surface interaction with the pigment supernatant, as indicated by the relatively large exotherm of -2384 microcalories. The latex serum also interacted with pigment surface, as shown by the larger exotherm of -944 microcalories. Both of these exothermic interactions indicated a greater dispersability of the latex particles with the pigment particles and helped make the free energy state thermodynamically more favored.

In contrast, for the nonuniform latex coating, there was significantly less interaction between the latex particle surface and the pigment supernatant, as shown by the endotherm of +153 microcalories. There was also less interaction between the latex serum and the pigment particle surface with an exotherm of -441 microcalories. From these more endothermic interactions, we would expect less dispersability of the latex with the pigment. From a thermodynamic view, the most favored condition probably would be that in which the latex particles would associate with themselves preferentially rather than associating with the pigment particles. As a result, the latex particles would have a propensity toward clustering. We also speculate that such a clustering phenomenon would result in a large exotherm, which would contribute to minimizing the free energy state.

CONCLUSIONS

Nonuniformity in the dispersion of the latex with the pigment in the wet coating color can result in a nonuniform distribution of the latex in the dry coating structure.

The nonuniformity of the latex distribution in the dry coating structure can result in nonuniformity of the printed image, such as back-trap mottle.

FUTURE WORK

Because preliminary results have shown that there are significant differences in the latex surface - pigment supernatant interaction for different degrees of latex clustering—further work is suggested to investigate how this interaction is affected by different latex processing conditions and modifications. In addition, further work is required to determine if there is a difference in the water retention property of the different wet latex coating colors with different degrees of latex clustering. This would help to establish how some water is "associated" between the pigment and latex and to what extent the water remains as bulk or "free" water [14]. This, in turn, could be used to elaborate further on the entropic aspects of the free energy thermodynamic relationship, as mentioned previously in the mechanistic discussion. Further work could also investigate the consolidation of these coatings.

From a commercial printing view, evaluations could be carried out to determine to what extent the web-offset performance is influenced by having different degrees of nonuniformity in the coating structure as a result of different degrees of latex clustering in the wet coating color. **TJ**

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INSIGHTS FROM THE AUTHOR

I chose this topic for my research since not a lot of previous work has been reported on the uniformity of wet coating color dispersions and I feel the industry could benefit from more scientific investigations in this area. This work supports previous work by Whalen-Shaw on using low temperature electron microscopy to visualize the different coating color components. My research differs in that, for the first time, the wet coating color dispersion uniformity of the latex particles with the pigment particles was investigated at high solids and for the corresponding effect on the dry coating structure and the commercial 6-color offset print quality.

To perform my research, a low temperature electron microscopy technique had to be developed to ensure that the aqueous phase of the wet coating color could be converted into a vitrous instead of a crystalline state, so that the coating color components could be fixed in their representative positions during cryogenic slicing as well as during the cryogenic transmission electron microscopy analysis. A technique was developed using liquid propane as the fast cooling cryogen; then, specific steps were developed during cryogenic slicing and viewing under the microscope to avoid water condensation and crystal formation, which adversely affects the imaging and resolution of the components.

One of the main discoveries was that latex particles and pigment particles can cluster with themselves and not disperse uniformly with each other. This work revealed that such a non-uniform dispersion of the latex with the inorganic pigment can influence the print uniformity of the dried coating structure.

In addition to other sources of non-uniformity such as drying conditions, mills can benefit from this work by also considering if non-uniformity of the dried coating is related to the dispersion uniformity of their wet coating colors. Further investigations could include the effect of different inorganic pigment types with different latex types on the wet coating color dispersion uniformity.

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Van Gilder

Print quality and the distribution of offset ink constituents in paper coatings

SANNA ROUSU, PATRICK GANE, AND DAN EKLUND

ABSTRACT: Little is known about the distribution of offset ink components in coated paper, although this is likely to be critical to print quality. This work focused on two fundamental processes that cause differences in distribution of ink constituents into a coating structure during printing. In the first, adsorptive chromatographic fractionation, chemical components of an ink mixture separate on contact with the paper coating due to their different adsorption characters. These differences arise from coating pigment chemistry, surface area, and morphology variables. In the second, latex-oil diffusion, molecular movement due to a concentration gradient takes place as oil molecules penetrate into the polymer latex matrix.

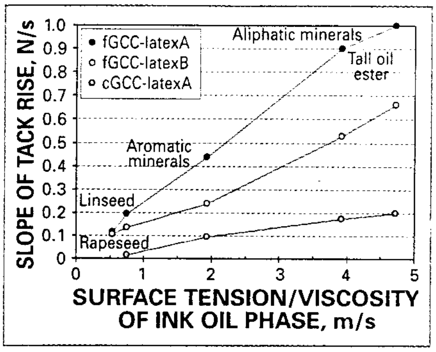
Our results indicated that adsorptive chromatographic fractionation, and the resulting distribution of ink constituents in a coating structure after printing, affected print quality parameters such as print gloss and density. Latex-oil diffusion and its constituents' distribution affected ink setting dynamics during printing, but did not influence print gloss or density. The inference is that adsorption onto the paper coating material surfaces delays permeation (sorption into the coating paper) of the slightly polar ink oils, hence delaying the concentration of solved ink resins on the ink-coating interface. Absorption through diffusion of ink oils by the paper coating latex internal matrix usually takes longer. In volumetric terms, it occurs away from the initial critical concentrating region of ink setting and cohesive ink tack build-up. Superimposed on these effects is the capillarity arising from the packing of pigments and binders.

Application: Mills, converters, and printers can use the results from this study in optimizing the coating formulations for desired print quality, and in understanding how different coating chemistry changes the printing result.

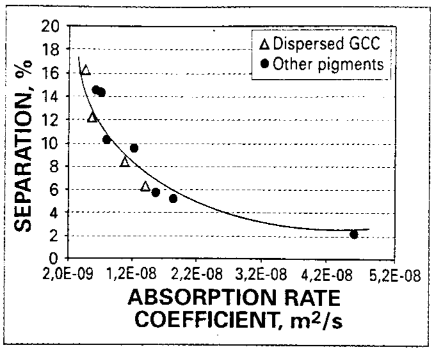
Achieving a high quality print, short and flexible delivery, with minimal environmental impact and minimal ink consumption, are continual challenges for both the paper and ink suppliers to the graphic industry. Problems originating from ink-coating interactions, such as ink and coating build-up on press blankets and mottle are major concerns associated with offset printing of coated paper [1]. The uneven absorption into paper and distribution of ink constituents in part accounts for these problems. There is a need for comprehensive understanding of the fundamental mechanisms controlling ink component distribution and its implication on print quality and defects, such as print unevenness and mottle, and press runnability, such as back-trapping, show through, piling, dot gain, set-off and rub-off. Both print quality and post-press functionality of coated papers are affected by the ink-paper interactions that occur over a wide span of time, ranging from the short time on the press to later converting and storage.

During the offset printing of coated paper, absorption of ink oils into the pores of the coating structure is an important process leading to ink setting and drying. With highly heterogeneous materials, such as paper and inks, absorption of ink into paper is not only dynamic but complicated because both chemical and physical phenomena occur simultaneously. Variables known to be important for processing and end-use properties, such as the absorption rate, state of the absorbent, and absorption path, are all interrelated. Capillary-driven transport is the major driving force for ink setting. Recent advances in this research area include adoption of the inertial flow mechanism to explain the rate dependency of the short time-scale absorption in small capillaries of low aspect ratio, like those of pigmented coating layer pores [2]. The absorption pattern is a complex function of the heterogeneous porous structure, leading to preferential pathways and thus not a fully pore-filled absorption-front during penetration [3]. Another mechanism of absorption involves chemical diffusion of ink fluid constituents into the latex portion or polymer matrix in the coating layer [4-6]. As offset inks are multi-component absorptive suspensions, characterization of absorption dynamics alone is not sufficient to describe ink-paper interactions resulting in variations in paper printability and print quality. Optimally, ink pigments and resins remain on the coated paper surface, allowing controlled release of the low-viscous fluid phase for absorption into the coating structure. Even low-viscosity ink components include a variety of chemically and physically differing constituents. The issue of fundamental interactions between ink and coating components, and their influence on the final distribution of a multicomponent ink on coated paper, has attracted some in-depth research during recent years [7-9].

This work was part of a larger study of the mechanisms behind the phase separation of offset ink constituents when in contact with coated papers [10]. In earlier publications, we identified the specific interactions between different types of offset ink oils and coating pigment [11] and the ink oil-coating latex interactions [12-13]. This paper highlights practical implications of these interactions by determining the effects on ink setting rate and paper print quality parameters, such as print gloss and density. It also shows how the various separating mechanisms affect print quality.



1. The rate of ink oil phase absorption into coated paper is determined mainly by the surface tension/viscosity ratio of the ink oil phase. A higher "slope of tack rise" value signifies faster ink setting (measured with the ISIT® instrument), which is here measured for ink-oil combinations marked in the figure and for three coatings made from coarse (cGCC) or fine (fGCC) ground calcium carbonate and SB latex types A or B [10].



2. The universal curve of separation of linseed and aliphatic mineral oils as a function of absorption rate over a range of porous pigmented coating structures [11] derived from different pigment types and particle sizes.

BACKGROUND

Parameters affecting ink setting rate

The oil phase of an offset ink is the primary component absorbing into the paper coating structure (**Fig. 1**). The oil properties, such as surface tension-to-viscosity ratio, control ink setting dynamics onto paper.

Today's offset inks are formulated from a wide range of oils and oil blends of mineral or vegetable origins. The chemical and physical properties of these oils vary considerably; some measured viscosities can range from 2 to 60 mPas. In effect, ink oil viscosity is the primary parameter affecting ink setting rate. Low viscosity oils, such as mineral oils, contain aliphatic components in preference to aromatic components and have a low boiling point. Those and treated vegetable oils, such as tall oil ester (from pine), lead to fast ink setting. Because of their high viscosity, untreated vegetable oils, such as linseed and rapeseed oils, are slow to penetrate coatings.

Only one variable—the oil type—was altered in the "controlled" inks presented in Fig. 1. Pigment and resin type and concentration were kept as closely constant as possible. Inevitably slight variations occur in ink oil release properties, mainly controlled by oil-resin compatibility, but those do not significantly contribute to absorption rate dynamics.

For a given oil surface tension-to-viscosity ratio, coating pigment and latex type strongly affect ink setting dynamics [10]. This is shown by comparing the three different coated paper types in Fig. 1, where the binder (latex) level was 10 parts per 100 (pph) by weight of pigment. The coating pigment type affects ink setting mainly through coating porous structure changes. Pigments characterized by small pore sizes, high air flow structure porosity, increased surface area, or low tortuosity result in fast ink setting rate [2, 3]. Latex properties—lower T_g and gel-%, and reduced solubility through monomer composition—also contribute to fast ink setting [4-6]. Latex, through its particle size, can affect the pore network packing of the coating layer and ink setting rate [5]. Overall, all three variables—ink oil type, coating pigment type, and latex type (at 10 pph)—may have an equally strong influence on the ink setting dynamics. However, the setting dynamic itself is controlled by the underlying physics and chemistry of the interacting ink liquid components and the coated paper surface.

Adsorptive chromatographic separation of ink constituents

A major portion of ink pigments and resins remain on the coating surface after ink setting, as observed physically and shown by the correlations in Fig. 1. Even so, the absorbed ink phase comprises a mixture of constituents with varied properties. Although these components are essentially miscible, their polarity may differ, ranging from practically non-polar mineral oil species to more polar vegetable oils and resins. Coating pigments can cause adsorption-controlled chromatographic separation of these chemically differing constituents during their absorption into the coating layer [11]. The hydrophilic coating pigment surface acts as a site for adsorption, and thereby retardation of the polar ink components, i.e. vegetable oils. On occasion, when the pores are very large, ink resins allow only the non-polar mineral oil species to absorb further into the structure [11].

For ink, polarity difference is the main property contributing to oil fractionation. Molecular size or viscosity difference is not a factor when considering species in a dissolved state (naturally, ink pigments and crystalline resin parts are excluded from absorption by size). For coating, the specific pigment surface area (m^2/g) is the most critical parameter describing the chromatographic separation activity of the solid phase, where increased separation is found to occur with larger specific surface area pigments, i.e. generally increasing with finer pigments [11].

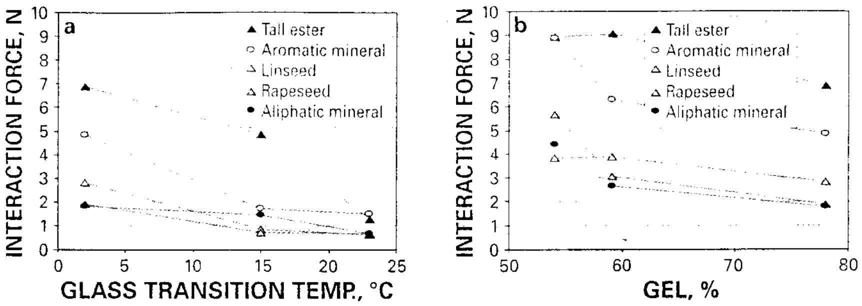
Increased pigment polar surface energy, mainly as a result of the amount and type of ionic dispersing agents used, also assists polarity-driven liquid separation. In addition to the influence from the pigment surface area and polarity, separation depends on the time frame available for adsorption-desorption interactions (**Fig. 2**). The rate at which the absorption front progresses through the porous structure is the critical universal parameter for the separation of a given oil mixture (linseed + aliphatic mineral in this case) over a range of pigment types and sizes.

In practical offset ink-coating contacts, the polarity differences driving separation of ink constituents are stronger at the initial stages of ink absorption, when the fine pores with large surface area are first exposed to the absorbed liquid. Separation is less complete in large pore size and highly permeable coatings, where the apparent absorption front progresses via drainage or percolation and there is a lack of surface area in the form of fine pores. With these types of coatings, occasionally in extreme cases, even ink resins may excessively penetrate into the coatings and cause scuffing, chalking, or other ink film related defects. Such coatings are formed mainly when pigment particle size distributions are too unimodal and coarse.

Diffusive differential ink oil – coating latex interaction

Ink oil diffusion into a latex polymer matrix is commonly acknowledged to be a significant mechanism affecting ink setting dynamics [4-6, 13]. At typical latex addition levels (~10 pph of latex per weight of pigment), the oil-latex diffusion is a secondary mechanism, mainly because it is a slower process than capillary-driven absorption. Significant oil-latex interaction may not be observed to influence ink setting if the capillary-driven absorption is itself very fast (as with very low viscosity oil and fine pore size coatings) [13]. Greater diffusion leads to faster ink setting, but as diffusion also leads to physical swelling of the latex polymeric matrix structure, some of the coating porosity can be lost. This further complicates predictions from absorption dynamics and affects the physical path of the ink constituent through a heterogeneous coating layer. The preferential chemistry of certain oils, which can adsorb onto pigments, means that the latex interaction assists removal of otherwise retarded oil components from the ink into the coating. This maintains a more even spatial distribution of the oils as a function of coating penetration, but not, of course, as a function of localized concentration differences in coating constituents.

Both the ink oil and the latex play a role in diffusion interaction. Oils with a high solubility parameter, such as vegetable oils and aromatic mineral oils, and low viscosity are most prone to diffusion. From the latex side, a less rigid/crystalline polymeric network, resulting from low T_g and gel %, and use of a monomer composition of low solubility parameter, has a greater tendency to take up ink oils and to swell [13]. Examples of the variation in interactions depending on latex T_g, gel %, and ink oil type are shown in **Fig. 3** (a) and (b).



3. The degree of oil-latex interaction depends on both the latex and oil properties, as shown here for a series of five oils and latex films of varying T_g and gel % [13]. The latex films are formed on a synthetic substrate and the interaction force is measured using the separation force method for applied oil on the ISIT device.

Product*	Supplier	Particle size, w/w% <2 µm	Particle size, w/w% <1 µm	BET area, m²/g
HC60	Omya AG	60	36	7.1
HC90	Omya AG	90	62	12.4
SC	Omya AG	97	80	16.1
CC	Omya AG	95	75	9.8
SW95	Imerys Ltd.	92	81	15.0
AG	Imerys Ltd.	94	83	21.0
AM90	Kaolin International BV	97	95	17.4
C10	FinnTalc	46	—	4.8
V40	Omya AG	85	63	8.8
A40	Specialty Minerals Ltd.	Median particle size	0.4	10.0

* HC stands for Hydrocarb, SC for Setacarb and CC for Covercarb – all product names of Omya AG – V40 is a costructure of carbonate and talc. A series of model latexes, L1-L9, and commercially available latexes were used. Details on the latexes are presented in Table II.

I. Details of coating pigments.

EXPERIMENTAL

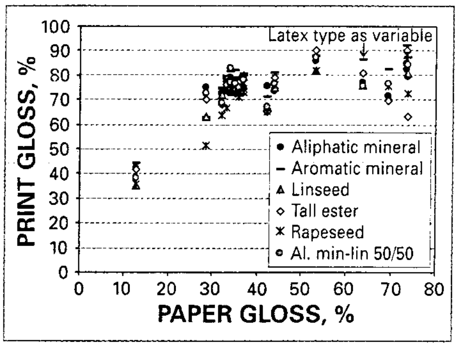
Coating and ink materials

The experimental approach, from which the early data also were drawn, is based on a systematic analysis of well-defined ink and paper coating systems. Model inks were made from the same ingredients as commercial offset inks. The one variable was the type of oil used. We studied an aliphatic mineral oil, aromatic mineral oil, linseed oil, tall oil ester, and rapeseed oil. We also tried oil mixtures containing 25%/75%, 50%/50%, and 75%/25% combinations of linseed and aliphatic mineral oils. The eight tested inks included approximately 45 w/w % of the respective ink oil or oil mix, 16 w/w % of cyan pigment, 10 w/w % of alkyd resin and 30 w/w % hard resin (supplied by Sicpa Oy, Finland). Coatings were formulated and applied with a coat weight of about 12 g/m^2 in laboratory scale on a smooth, non-absorbent synthetic base sheet (Synteape; currently Oji-Yuka under the Yupo brand) to have a macroscopically homogeneous coating structure. Pigment and latex types were studied at a constant latex addition level of 10 pph by weight of pigment to control changes in coating structure and chemistry. Pigments included ground calcium carbonates (GCCs) with different particle size distributions, clays of different geographical origins, talc, and precipitated calcium carbonate (PCC). They were investigated with a constant type of styrene-butadiene copolymer (SB) latex (**Table I**). Latexes were further investigated by including nine experimental types, with controlled properties, and several commercial grades (**Table II**), which were each blended with a constant GCC pigment. The structures were analyzed with mercury porosimetry (AutoPore III,

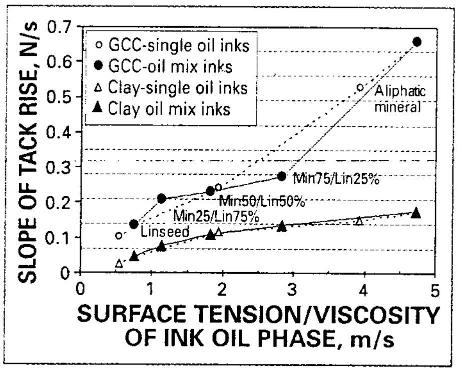
Abbreviation	Supplier	Monomers	T_g, °C	Gel, %	Particle size, nm
L1	BASF AG	SB	2	78	156
L2	BASF AG	SB	6	59	155
L3	BASF AG	SB	1	54	159
L4	BASF AG	SB(Acn)	12	70	148
L5	BASF AG	SB	15	78	155
L6	BASF AG	SB	23	77	152
L7	BASF AG	SA	7	65	153
L8	BASF AG	SA	24	59	156
L9	BASF AG	SA(Acn)	6	79	153
DL940	Dow Chemical	SB	22	—	140
DL980	Dow Chemical	SB	-7	—	130
S360D	BASF AG	SA(Acn)	5	—	—

SB = styrene-butadiene copolymer; SA = styrene-acrylate copolymer; Acn = acrylonitrile monomer added in an SB or SA.

II. Details of model and commercial latexes.



4. Print gloss (inks based on the oils named in the legend) dependence on sheet gloss. Coatings were based on varying pigment and latex type and they were applied on micro-smooth base sheets.



5. Ink setting is determined by the surface tension and viscosity properties of the absorbing oil phase both in the cases of single oil and multi-oil inks. Thus, chromatographic separation of polar and non-polar ink oils during absorption does not observably affect the initial ink setting dynamics at 10 pph latex addition level.

Micromeritics) and corrections applied using Pore-Comp [14]. Coated papers were studied in their uncalendered state.

Ink setting rate

Ink setting was characterized as ink-on-paper tackification using the ISIT® laboratory tester (SeGan Ltd, UK). The ISIT method provides an analysis of the ink-paper interaction from the initial tack rise, caused by the ink fluid phase absorption into the coating structure, until the consolidation of the ink layer. The slope, or tack rise rate (N/s), is used as a measure for the mainly capillary-driven ink oil uptake by the coating. We followed a standard procedure of ink application from a roller on the ISIT, pre-inked using an IGT ink distributor, for printing onto the coated paper samples. Three repetitions were performed for each ink-coating combination. A more detailed description of the device hardware and analysis procedure can be found in the literature [15].

Print quality

Print gloss and density were measured from a full-tone cyan surface-printed for the ISIT measurement strips of paper. The ink layer thickness was constant, approximately 1 g/m². The gloss of coated paper before and after printing was measured using the TAPPI 75° Standard (T 480, om-92). Print density was measured using a standard optical measurement technique (D186, GRETAG).

RESULTS AND DISCUSSION

Surface topography and print quality

To reveal the contribution of either the differential distribution of ink constituents through adsorption chromatography or the latex-oil diffusion (or both) on print quality, the strong surface topographic contribution needs to be excluded. Paper gloss (micro-smoothness) of the paper coating is known to be a critical factor for offset printed gloss [16]. **Figure** 4 shows the print gloss-paper gloss relation for all tested combinations of coating pore structure and chemistry, as well as different inks. Higher sheet gloss leads to higher print gloss. However, we observed up to 20 units difference in print gloss for certain coating-ink combinations with constant sheet gloss.

In addition, print gloss does not infinitely increase with sheet gloss. Above a maximum sheet gloss of approximately 33%-35%, the ink cannot further "smoothen" the coated paper surface and therefore cannot produce "optically" ever-increasing gloss. Above the critical sheet gloss, the snap (delta of print and paper gloss) actually decreases with smoother paper surface, presumably because of reduced coating pore size. The same has been found by Donigian *et al.* [17] and has been explained by the faster ink immobilization associated with finer pores. Faster immobilization allows a shorter time for ink filament leveling after the ink film split during its application, causing a rougher, less glossy print [9, 18]. Additionally, refractive index changes occur in the ink on paper as a function of setting time and aging [19]. To understand the variation in print gloss beyond the dependency on sheet gloss, and hence independently of paper smoothness, print gloss data were normalized for paper smoothness by dividing the delta gloss (print-sheet gloss) with paper gloss.

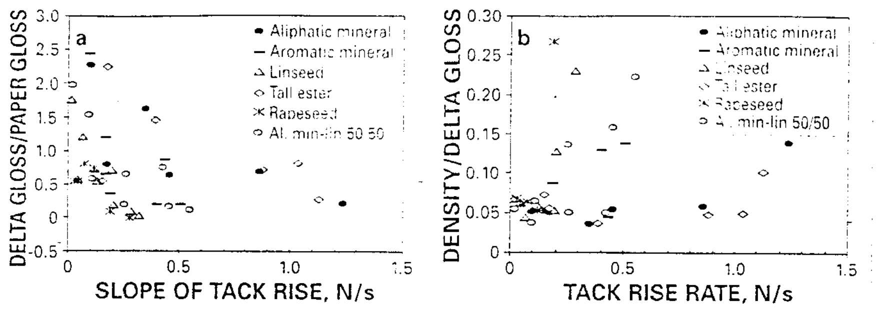
Print density is primarily affected by the ink layer thickness and smoothness, which is a function of both ink (e.g. pigment concentration) and coated paper surface properties, and their interaction. With a given type and amount of ink (in g/m²), a smoother paper creates higher print density; or a greater amount of ink is required to reach a desired print density with a silk/matte grade than with a glossy paper. As shown previously [16], the paper surface roughness also strongly influences the contour of the printed ink film, or print gloss. Therefore, print gloss and density are strongly related parameters. Similarly to print gloss, the print density values were normalized to print gloss to extract and identify influences of the specific ink-coating interactions, independently of surface topographic and ink smoothening effects. This was effectively achieved by dividing the print density data by delta gloss.

Adsorption chromatography—influence on print quality

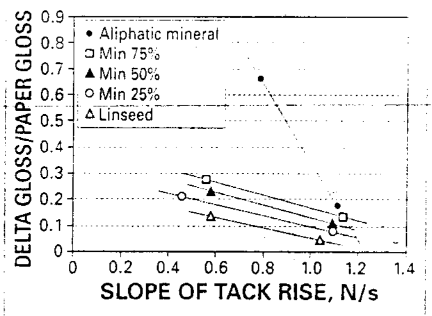
We first considered the influence of adsorption-driven chromatographic separation of ink constituents on ink setting rate. We did this by comparing the ink setting rate for a series of inks formulated first with only one oil type and then with a series of inks composed of a mixture of two oils that are known to fractionate (linseed and aliphatic mineral oils in 1:3, 1:1, and 3:1 proportions). As seen in **Fig. 5**, there is similar absorption behavior in both cases. Therefore, adsorption chromatographic separation does not influence the absorption behavior during ink setting, at least not in a macroscopic scale when measured with ink tackification.

The final normalized print gloss (a) and density (b) are plotted against the ink setting rate in **Fig. 6** for different combinations of inks and coatings having variable pigments. Tack rise rate affects the normalized print gloss and density differently for each ink; with a given ink setting rate as defined by the coating structure, gloss and density depend on ink type. From data normalized for topographic differences between the paper and print, considered here as a function of the absorption rate dependency of the coating, we conclude that it is indeed the spatial location of the oil in the coating and ink layers that causes the final print gloss and density differences.

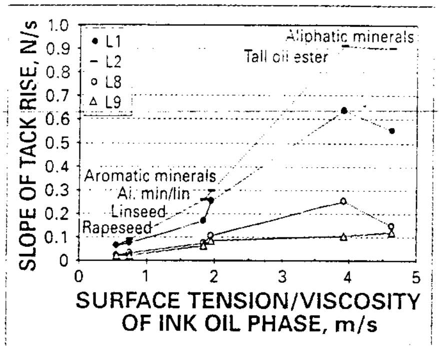
Comparing the normalized gloss data for a series of inks prepared with different proportions of linseed and aliphatic mineral oils (**Fig. 7**), we can see that adsorptive chromatography is one mechanism contributing to gloss and density related variations. Inks separate according to their categories, and the gloss values change consistently with the original mineral-to-linseed oil ratio in the ink. By extrapolating, we can conclude that a more efficient separation of the oils in a slower setting coating may result in higher print gloss.



6. Influence of ink oil removal rate on (a) print gloss, and (b) density as normalized for the paper and additive print gloss respectively. Coatings are formulated with a series of different pigments and 10 pph of given latex.



7. Oil properties and their distribution in the coating layer affect print gloss development and may be the cause of gloss related mottle. This series of inks with varying aliphatic mineral oil and linseed content were printed on two different coatings with varied pigment, one a fine GCC (fGCC) (faster tack rise, i.e. greater value of tack rise), the other an English clay (slower slope of tack rise).



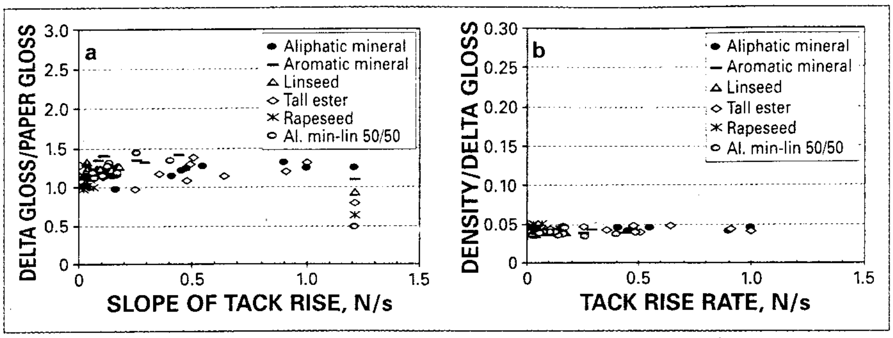
8. Oil absorption from an ink measured as ink tackification on coated sheets with varying latex grade (fGCC, 10 pph of latexes L1, L2, L8, and L9 respectively; see Table II) is controlled by the surface tension and viscosity properties of the ink oil-phase. The influence of differential oil-latex interaction is observable with strongly latex-interacting oils, namely aromatic mineral and tall ester oil-based inks, as a discontinuity at surface tension/viscosity ratios of about 2 m/s and 4 m/s.

Therefore, the distribution of ink oils in a coating structure due to chromatographic separation leads to print gloss and density variations in the print. Oils are drawn out differently from ink by coatings having different pigment types, creating differences in print gloss and density values. On a heterogeneous paper, this may lead to spatial variations in the plane of paper, which could be seen as mottle or print gloss unevenness.

Oil distribution in latex and the influence on print quality

Figure 8 addresses the latex-oil interaction effect on ink setting dynamics. With respect to ink chemistry, the viscous properties of the ink oil phase still strongly dominate ink setting dynamics, although slight deviations in the correlation are observed with the strongly latex-interactive tall ester and aromatic mineral oil-based inks. Variations originating from the coating latex type are, however, much larger.

Figure 9 shows the normalized print gloss (a) and density (b) data plotted against initial ink setting rate variations caused by latex-oil interaction. We note that print quality is independent of ink type. Differences in the distribution of ink oils in the latex matrix do not influence the average print quality.



9. Influence of ink oil removal rate on (a) print gloss, and (b) density as normalized for the simultaneous paper gloss and delta gloss development respectively. Coatings are formulated with fine GCC pigment and a series of varied latexes at 10 pph. The inks contained the oils named in the legend.

This conclusion does not imply that latex type has no significant influence on print quality—the opposite was seen already in Fig. 3, where significant differences were observed, depending on latex type. Results in Fig. 9 rather confirm that final print gloss and density are not affected by preferential uptake of a certain type of ink oil by the latex polymer matrix. The interpretation is that distribution of ink oils within the latex polymer matrix of the coating structure is similar for all oil types, or at least it is insignificant in affecting the average print quality, despite significant differences in the magnitude of interaction and ink setting dynamics. Large print gloss and density variations may nevertheless result, depending on latex type, surface topographical variability, coating structure, and coating component distribution.

CONCLUSIONS

The distribution of offset ink constituents as the ink comes in contact with a coated paper during printing influences ink setting rate and final print quality. Distribution variations arise from interactions with the coating pigments and with latex. Our main observations can be summarized as follows:

Adsorptive chromatographic separation of ink oils and latex-oil diffusion both affect how ink constituents distribute in the coating layer. This consequently affects the final print quality.

Coating pigment type and surface area control the polarity-driven chromatographic fractionation of ink constituents and influences print density and print gloss. Adsorption slows down absorptive permeation of polar oils.

Coating latex-oil diffusive interaction affects ink setting rate, but it does not influence the print gloss or print density. Absorption through diffusion into the coating latex polymer matrix usually increases preferentially the rate of uptake of weakly polar ink oils by the coating. Diffusive absorption is viewed as distinct from initial latex packing effects in the pore network structure, which clearly affect capillarity, though swelling and blocking may be a consequence. Both interactions are time-dependent, and their relevance depends on the total time available. The time available depends on the total absorption dynamics of the coating, which is affected by both physical and chemical sorption of ink oils into the coating. Generally, adsorption has more relevance in short time scale, fast setting situations, whereas the influence of latex-oil diffusion occurs on a longer time scale.

In a heterogeneous paper structure, the phenomena described above occur simultaneously, but spatially distinct, and can be responsible for print unevenness, mottle, or print smoothness and gloss variations.

These observations suggest that paper print quality deteriorates as a result of the separation of weakly polar and non-polar ink oils in a coating layer, if associated with a strong retardation of the polar oil. This is interpreted as being due to adsorption of the polar resin-solving component onto the pigment, leading to deterioration of average print quality. Enhanced absorption of polar components, which may occur through absorptive diffusion within the latex binder, reduces the effect of fast ink setting rate on print gloss and print density. This leads to the conclusion that a too rapid differential concentrating of the ink via a too rapid non-polar mineral oil loss, for example, leads to a retained solved resin within an otherwise immobilized ink layer. This can result mechanically in shrinkage and roughening effects during subsequent resin concentration within this initially immobilized matrix structure. Maintaining the right balance of polar and non-polar oils within the concentrating ink layer is therefore critical.

We must point out that our observations do not take into account the impact of multiple nip impressions, as would occur on a multicolor press. The action of rapid ink setting under dynamics of film splitting can act to alter the conclusions, with respect to the relative roles of adsorptive separation versus absorptive diffusion. However, the condition of the single color before multiple nipping is defined by the observations made here. **TJ**

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INSIGHTS FROM THE AUTHORS

There is little fundamental knowledge available on the molecular level interactions between ink and coating chemicals. This information is, however, known to influence the printability and print quality.

This work is part of a larger PhD project and series of publications (listed in the reference list in the article). This part of the work concludes the final implications of molecular level interactions studied in earlier parts of the work, and is thus the last piece.

One of the challenges in completing this study was the difficulty in separating single elements of molecular level phenomena and print quality attributes. It was accomplished by using a systematic approach in choosing chemicals and by normalizing the final result data for different aspects at a time.

The knowledge from this study can be used in optimizing the coating formulations for desired print quality, and in understanding how different coating chemistry changes the printing result.

Further work in this area is being continued at Åbo Akademi University by other researchers.

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Influence of the Binder Thermomechanical Properties on the Fixing Process and Structure of Dry Surface Treated Papers

K. PUTKISTO, J. MAIJALA, J. GRÖN and M. RIGDAHL

In the dry surface treatment (DST) of paper, the coating formation onto the paper surface is through electrostatic deposition of charged coating particles and compression and fixing of the layer through calendering. The effects of binder content and viscoelasticity on the development of the pore structure and the strength of the coating were studied in relation to the transient fixing process. The coating particles were prepared by freeze drying of pigment–latex suspensions. Latexes with a high softening temperature and high elasticity above the softening temperature gave a lower degree of particle aggregation, which thus enabled a higher homogeneity of the coating, a more efficient packing and reduction of large voids. The DST fixing seemed efficient in the densification of the surface layer of the coating and gave a more open interior. Reducing the number of large pores is essential with respect to optimizing the permeability and absorption properties of the coated papers.

Lors du traitement de surface à sec du papier, la couche se forme à la surface du papier par le dépôt électrostatique de particules de sauce de couchage chargées, et par la compression et la fixation de la couche lors du calandrage. Les effets de la teneur en liant et de la viscoélasticité sur le développement de la structure des pores et la résistance de la sauce de couchage ont été étudiés en rapport avec le processus de fixation transitoire. Les particules de la sauce de couchage ont été préparées en lyophilisant des suspensions de pigment–latex. Les latex dont la température de ramollissement est élevée et qui possèdent une forte élasticité au-dessus du ramollissement présentaient un plus fort degré d'agglomération, ce qui a permis d'obtenir une meilleure homogénéisation de la sauce de couchage, un tassement plus efficace, et une réduction des grands vides. La fixation du traitement de surface du papier a semblé efficace en matière de densification de la couche de sauce en surface et a offert un intérieur plus ouvert. La réduction du nombre de grandes pores est essentielle si l'on veut optimiser les propriétés de perméabilité et d'absorption des papiers couchés.

INTRODUCTION

The dry surface treatment (DST) provides a combined process for coating and smoothing a paper surface. By applying the pigment coating materials in a dry powdered form and anchoring the coating layer to the paper surface in a subsequent thermomechanical fixing phase, the drawbacks related to the presence of water in conventional suspension coating can be avoided. The technique is described in more detail by Maijala et al. [1]. In a simplest case, the DST coating contains two components, the pigment and the thermoplastic polymeric binder, both prepared in a dry particulate form.

The conditions and time scale of processing coating materials during DST differ significantly from the ones used in conventional suspension coating techniques in the production of pigmented paper. Firstly, an electric field is used to direct charged coating particles onto the paper surface, where the deposited layer attaches mainly electrostatically. Secondly, during the heating and compression (fixing) phase, the coating binder should soften sufficiently and attach the coating layer to the fibrous substrate, as described by Putkisto et al. [2–4]. The dwell time in the heated roll nip, being only a fraction of the time for polymer film formation during drying with wet-laid coating techniques, is adjusted to give the polymeric particles sufficient time to sinter but not to result in excessive flow that may give irregularities in the component distribution. For the coating layer to sustain the stresses imposed during the surface treatment process and in subsequent converting stages, the binder distribution should be homogeneous and provide an adequate cohesion of the coating as well as adhesion characteristics.

In our previous studies on the properties of the pigment-coated DST papers [1–4], the mechanical strength of the coating and its adhesion to the substrate were due mainly to the relatively high polymer (binder) content used. However, a high binder content may give several disadvantages, both in terms of processability and in terms of performance. An increased binder content may seal the pore structure of the coating and thereby impair the printing properties of the layer through a reduced absorption capability. When preparing the coating particles by drying a suspension and subsequent grinding, the particle size obtained

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seemed to increase with increasing binder content, due to a pronounced aggregation and, presumably, to a lower disintegration capability of grinding [2–4]. To achieve a coating layer of uniform structure and to reduce the aggregation tendency, the binder in the particle aggregates should exhibit sufficient flow and molecular diffusion across the interface between the aggregates. This should be achieved during the fixing phase of the DST. A high binder content (20 parts per 100 parts of the pigment (pph) and higher) and aggregation were also associated with an increased sticking tendency of the coating to the heated roll surface [1,2,4]. Additionally, in dry two-component DST coatings (containing pigment and binder), the binder accounts for the largest part of the material costs. Thus, by lowering the binder content, the costs could be reduced markedly.

In several cases, achieving the optimum combination of the properties of the DST coating binder and of the fixing parameters has been critical with regard to the bonding of the coating and the surface strength [2,3]. The critical issue is thus related to improving the mechanical strength of the dry-formed coatings without an excessive amount of binder. In previous studies [2], the void volume and the dominating pore size of the DST coatings were noted to be rather high (void volumes of 40–55% and pore sizes close to 0.5 µm) in relation to those of typical wet-coated papers (void volumes of 30–35% and pore sizes close to 0.1 µm). Therefore, it was assumed that, by adjusting the fixing nip impulse, i.e. the roll temperature, the load and the dwell time in the nip, a higher compression and a greater degree of binder flow and thus a finer pore structure and enhanced adhesion to paper surface could be obtained. Both a higher cohesion and a better contact with the base substrate would improve the mechanical properties of DST papers. In this work, the effects of the viscoelastic properties of the polymeric binder, the binder content and the fixing conditions in the heated nip are discussed in terms of the coating structure and performance. Besides the process conditions, the size of the coating particles has a strong bearing on the coating performance.

TABLE I
COATING COMPONENTS

Component	Average particle size, µm	Glass transition temperature, °C	Gel content
GCC Hydrocarb 90, OMYA Oy, Finland	0.65	–	–
51-H, carboxylated latex based on S/B copolymer, Dow Chemical Co., Dow Finland	0.18	51	High
45-M, carboxylated latex based on S/B copolymer, Dow Chemical Co., Dow Finland	0.19	45	Medium
20-H, carboxylated latex based on S/B copolymer, Dow Chemical Co., Dow Finland	0.14	20	High
Pigment dispersant, sodium salt of poly(acrylic acid) Dispex N40, Ciba Specialty Chemicals Finland Oy	–	–	–

TABLE II
PARTICLE COMPOSITION AND SIZE

Pigment, pph	Binder, pph			Aggregate size, µm	
GCC	51-H	45-M	20-H	D90	D50
100	10	0	0	11.3	2.3
100	0	10	0	9.5	2.7
100	0	0	10	26.7	10.1
100	20	0	0	16.4	3.9
100	0	20	0	16.9	3.6
100	0	0	20	44.8	17.1

EXPERIMENTAL

Coating Components and Properties of the Coating Powder

Ground calcium carbonate (GCC) was used as the pigment and three grades of carboxylated latexes based on styrene–butadiene (S/B) copolymers with various softening behaviours were used as binders. Table I includes the average particle size of the particulate components, glass transition temperature (T_g) and gel content, related to the cross-linking of the latex polymer. The T_g values were determined by differential scanning calorimetry (DSC, Perkin Elmer Pyris 1, Rodgau-Jügesheim, Germany) at a heating rate of 10°C/min.

The viscoelastic properties of the polymeric binders were evaluated using dynamic mechanical analysis (DMA) (ASTM D5279) [5] at a frequency of 1 Hz. The samples were prepared by compression moulding.

Coating particles were prepared by freeze drying a pigment–latex suspension, mixed at a solids content of ~50 wt% with 0.04 pph of the dispersing agent and subsequently grinding the dry, flaky particle aggregates with a laboratory grinder. The particles were immersed in liquid nitrogen during the grinding to avoid softening the binder. The composition and the particle (aggregate) size distribution of the coating particles used are given in Table II. The particle-size distribution was determined in the dry state using low-angle laser light scattering (LALLS, Malvern series 2600c, Malvern, UK). D90 and D50 denote that 90 and 50% by volume, respectively, of the particles were smaller than the given size.

DST of the Papers

The laboratory-scale DST equipment with a powder feeder, a deposition unit and a fixing unit, a thermomechanical treatment employing a soft-nip calender, has been described in detail in [1]. The base paper was a wood-containing paper with a grammage of 45 g/m^2. The ingoing moisture content of the base paper was kept at 6% throughout the trials. One-sided coated DST papers were produced with a coat-weight of ~6 g/m^2.

During the fixing phase, the papers were compressed in the soft nip of a laboratory calender consisting of a heated roll with a Teflon-based cover at 200°C and a rubber-covered backing roll. This process is called pretreatment in the following. A machine speed of 10 m/min and a linear load of 45 kN/m were used, corresponding to a dwell time of 60 ms. For reinforced fixing, a soft nip of a laboratory calender consisting of a heated roll with a hard-chromed surface and a polymeric backing roll was employed. The roll surface temperature was 200°C, the linear load ranged from 20 to 50 kN/m and the machine speed from 10 to 30 m/min, corresponding to nip dwell times of 20 and 6 ms. Reinforced fixing was accomplished with two passes in the nip.

For some papers, a thermal post-treatment to improve the binder flow further in the coating was used. The post-treatment temperature was 150°C, without a mechanical load, and the dwell time ~90 s.

Coating Coverage

The coating coverage was assessed with image analysis from micrographs obtained using environmental scanning electron microscopy (ESEM) (ElectroScan 2020, Hillsboro, USA with an Oxford Tetra solid state backscatter electron detector, Oxford Instruments, Ltd., Buckinghamshire, UK).

In some cases, the covering ability was also examined by the burnout technique, described e.g. by Engström and Lafaye [6], in which the specimen is immersed in a solution of 25 g/L of ammonium chloride in a mixture of 1:1 by volume of ethanol and water. After saturation with the solution, the specimen is allowed to dry at room temperature and is then placed in a ventilated oven at 200°C for a few minutes. At this temperature, the fibres in the paper turn black but the inorganic pigment remains white. The distribution of the pigment on the paper surface then can be assessed with a microscope (ZEISS Axioskop 40, Göttingen, Germany).

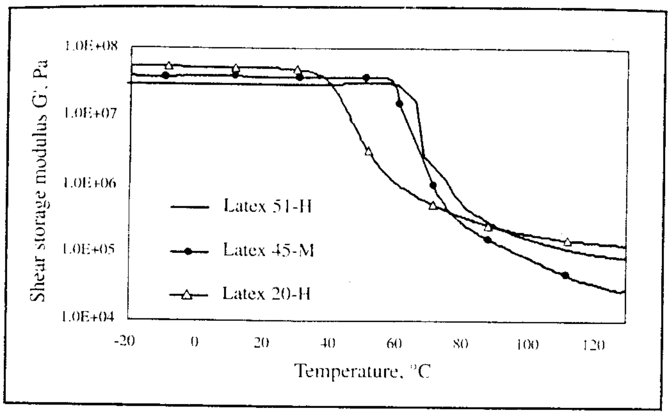

Fig. 1. Shear storage moduli of the binders as functions of temperature at a frequency of 1 Hz.

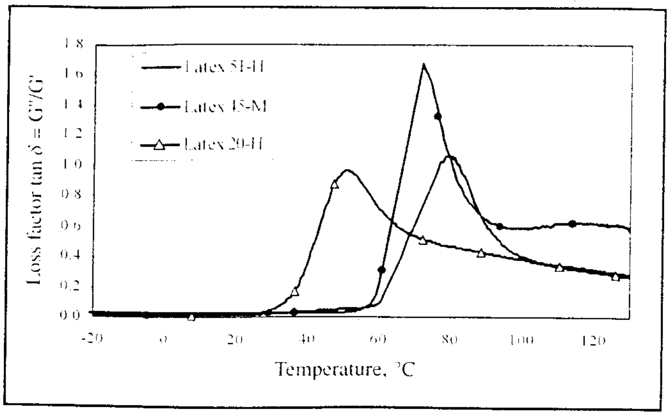

Fig. 2. Loss factors in shear mode of the binders as functions of temperature at a frequency of 1 Hz.

Coating Structure and Interlocking with the Paper Surface

The coating surface was examined with SEM (Philips XL-30, Eindhoven, the Netherlands) after coating the surface with a thin layer of carbon. For SEM examination of cross-sections, the samples were embedded in an epoxy resin (Epofix from Electron Microscopy Sciences, Hatfield, PA, USA), followed by finishing with appropriate grinding and polishing.

The coating/substrate interphase and the coating penetration were examined by SEM of such cross-sections. We also studied the interphase region by extracting away the fibres from the coated papers with a method described by Dickson and Lepoutre [7], using a cupriethylenediamine solution and SEM.

The porosity of the coating layers papers and their pore-size distributions were evaluated by mercury porosimetry (AutoPore III 9410CE, Micromeritics, Norcross, GA, USA).

Paper Properties

The following standard testing methods were used: grammage and coat weight (ISO 536:1995) [8], moisture content of the base paper (ISO 287:1985) [9], Bendtsen air permeability (ISO 5636-3) [10], PPS-s10 surface roughness (ISO 8791-4) [11], gloss (ISO 8254-1) [12] and IGT surface strength (ISO 3783:1980 with a standard low-viscosity oil) [13]. In addition, oil absorption with a nozzle applicator (Keskuslaboratorio Oy, Espoo, Finland) with a low-viscosity mineral oil and Ink Surface Interaction Tester (ISIT, SeGan Ltd., Cornwall, UK) with a fast-setting offset ink (Rapida FW 7000 by Huber Group, Hostmann-Steinberg Ltd., Toronto, ON, Canada) were used. With the ISIT, the printing speed was 0.5 m/s and the linear load in the ink transfer roll nip was 10 kN/m. All measurements were performed on specimens that had been conditioned according to ISO 187:1990 [14] at 23 ± 1°C and 50 ± 2% relative humidity.

The reference paper used here was a blade-coated and soft-calendered machine-finished coated paper with a total grammage of 54 g/m^2 with a coat weight of ~6.5 g/m^2 per side.

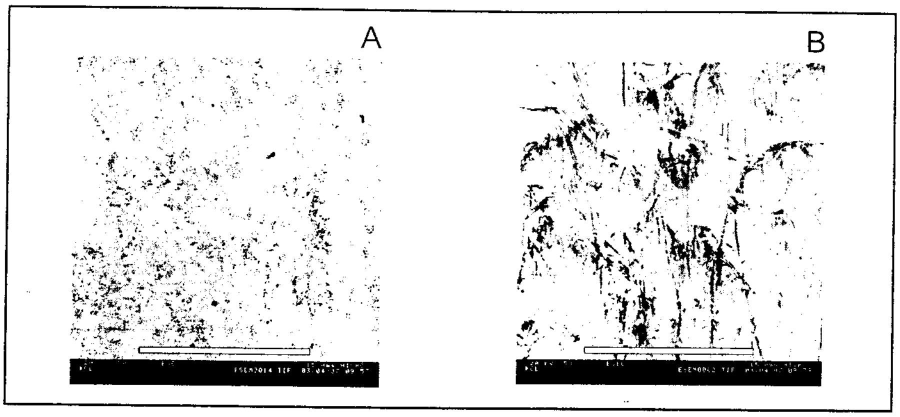

Fig. 3. ESEM surface micrographs of (A) a DST paper, coated with 100 pph GCC + 10 pph latex 51-H, fixed at 30 m/min with 20 kN/m, and (B) the reference paper. Scale bars = 1 mm.

RESULTS AND DISCUSSION

Binder Viscoelastic Properties

The S/B copolymer binders used had different glass transition temperatures and gel contents which, as expected, affected their viscoelastic properties as revealed by DMA. Figures 1 and 2 show the shear storage modulus G′ and the mechanical loss factor tan δ as a function of the temperature of the various binders. The binders with a higher degree of crosslinking and thus a higher gel content, i.e. latexes 20-H and 51-H, exhibited higher elasticity at elevated temperatures, exceeding T_g, than latex 45-M. An enhanced degree of flow of a less crosslinked polymer, expressed in a somewhat simplified manner, can be associated with a relatively low value of G′ and high level of the loss factor in the rubbery region at elevated temperatures, as was observed with latex 45-M (Figs. 1,2).

The relation between the viscoelastic properties of the binders and the performance of wet-coated papers during calendering has been discussed, for example, by Wikström et al. [15] and Mikkilä et al. [16]. It was noted that increased elasticity of the binder (higher G′) may contribute to reducing the formation of coating sticking deposits on the calender roll but that a certain degree of viscous flow is required to achieve permanent deformation of the coating layer, advantageous for improving the surface smoothness, for example.

An increased elasticity of the binder reduced the tendency for sticking during the DST fixing phase also [2], but the particle (aggregate) size also was important for the mechanical strength of the coating layer, as will be discussed later. When the coating particles are prepared by drying and grinding, a relation between the binder softening temperature and the aggregate size can be found [2]. The low-T_g latex 20-H appeared to increase the particle aggregation compared to the other two latexes.

Coating Coverage

Figure 3 shows the coating surface structure for a DST paper and the reference paper on the millimetre scale. The average coverage value, obtained with image analysis from five images of each sample, for the DST papers ranged between 89 and 95%, whereas an average of 87% was obtained for the reference. Image analysis with Euclidean Distance Map technique enabled evaluation of the size of the uncoated areas (characterized by a factor with units of µm^2) also. For the reference paper, the size of the uncoated areas were markedly larger than those observed for the DST papers and, on the average, the corresponding factors describing the size of the uncoated areas were 24 and 2.5 µm^2, respectively.

In Fig. 4, the surface structure of the DST coatings and of the reference were compared using light microscopy on a 10–100 μm scale after the burnout treatment. The fibres, which were darkened by the treatment, can be distinguished through the coating layer. Compared to the DST papers, the surface fibres of the reference paper showed through on the entire examined area. On the other hand, the variation on this scale, both in the coating coverage and surface porosity, was higher for the DST papers, which also exhibited differences depending on the coating composition. The homogeneity of the coatings with high gel latexes appeared to be lower, as reflected in a more open surface with some visible pores. The relatively large aggregate size of the coating particles containing latex 20-H seemed to give an aggregated structure in the coating layer also, although the polymer formed a film on the surface (Fig. 4). Holes due to coating sticking or poor levelling were attributed mainly to particle aggregation.

Coating Structure Examined Using SEM

SEM analysis of the coated surfaces revealed differences in the surface structure also between the DST papers and the reference. There seemed to be a higher variation of the surface density of the DST coatings (Fig. 5), resembling the variation in the roughness or topography of the fibrous surface. It may be assumed that this variation is caused by the corresponding differences in local pressures acting on the fibre surface during the fixing stage. However, the coating surface appears smooth. For the reference paper, the fibre outline can be discerned through the coating layer, but the surface appears uniform. At a binder content of 10 pph, the DST coatings with high-T_g latexes appeared to be more uniform due to diminished aggregation and the lower amount of sticking deposits compared to the coatings containing latex 20-H.

A higher binder content, 20 pph, resulted in a stronger aggregation of the particles and, as a consequence, not only an aggregated coating structure (Fig. 6) but also an increased amount of sticking deposits with all latexes used. A pronounced sticking tendency was observed, especially at longer dwell times.

The densifying effect on the surface of an increased linear load during the DST fixing process is shown in Fig. 7, where the two coatings have been fixed at a similar speed but with a linear load of either 20 or 50 kN/m.

In the cross-section, the differences in the structures of the coating layers between the DST papers and the reference paper appeared to be small when the DST coating particles were small, i.e. with latexes 51-H (Fig. 8A) and 45-M (Fig. 8C). However, with increased particle size (latex 20-H), the coating layer was less uniform in thickness (Fig. 8B), and detachment of sticking deposits was obvious. On average, the DST papers exhibited a smaller variation in the coat weight and a higher surface smoothness than the reference paper.

At the higher binder content, the

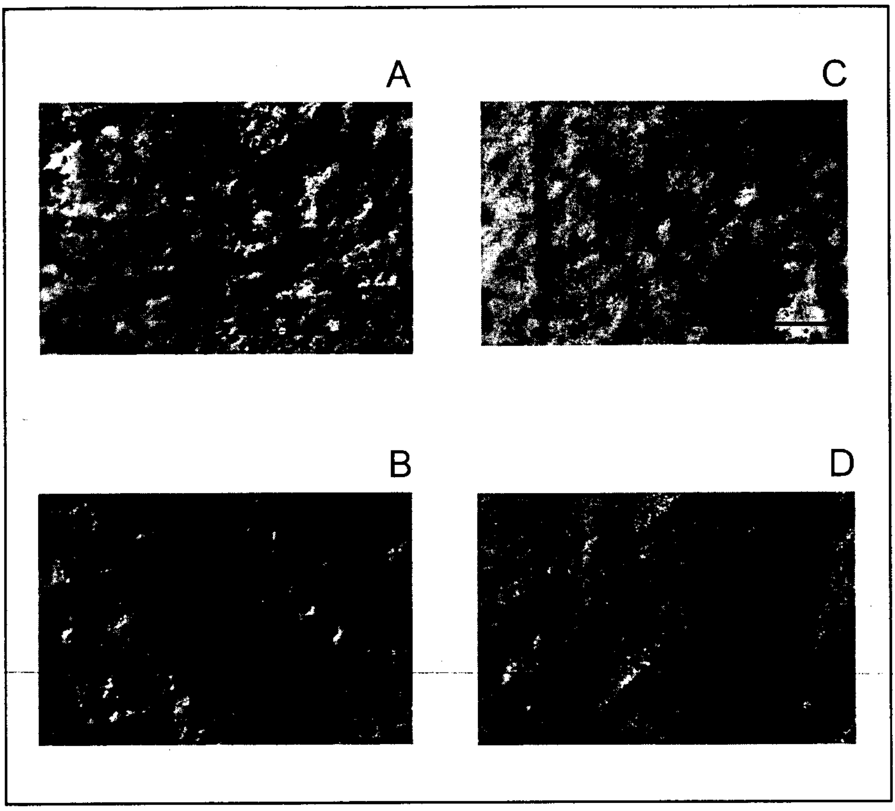

Fig. 4. Light microscope images of burnout-treated DST papers, coated with (A) 100 pph GCC + 10 pph latex 51-H, (B)100 pph GCC + 10 pph latex 20-H, (C) 100 pph GCC + 10 pph latex 45-M, fixed at 10 m/min with 20 kN/m, and (D) the reference paper. Scale bars = 200 μm.

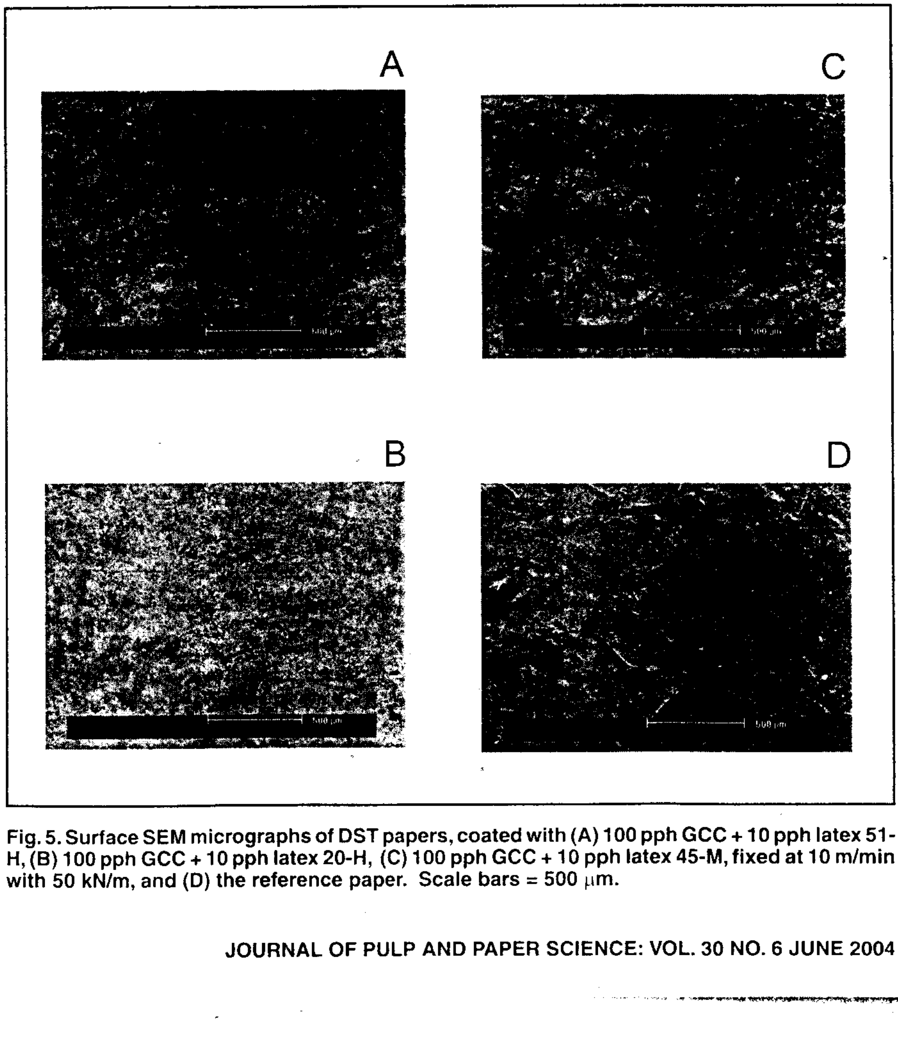

Fig. 5. Surface SEM micrographs of DST papers, coated with (A) 100 pph GCC + 10 pph latex 51-H, (B) 100 pph GCC + 10 pph latex 20-H, (C) 100 pph GCC + 10 pph latex 45-M, fixed at 10 m/min with 50 kN/m, and (D) the reference paper. Scale bars = 500 μm.

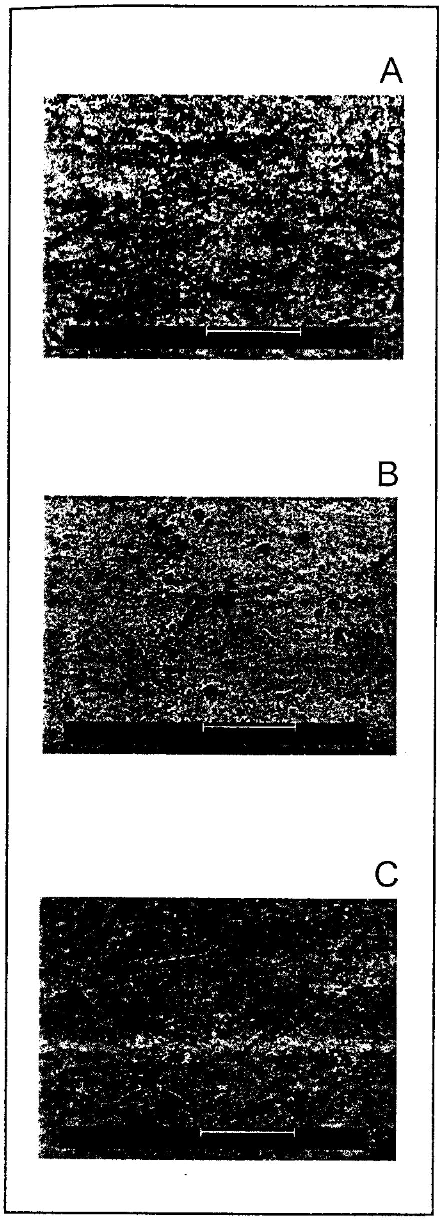

Fig. 6. Surface SEM micrographs of DST papers, coated with (A) 100 pph GCC + 20 pph latex 51-H, (B) 100 pph GCC + 20 pph latex 20-H and (C) 100 pph GCC + 20 pph latex 45-M, fixed at 30 m/min with 20 kN/m. Scale bars = 500 μm.

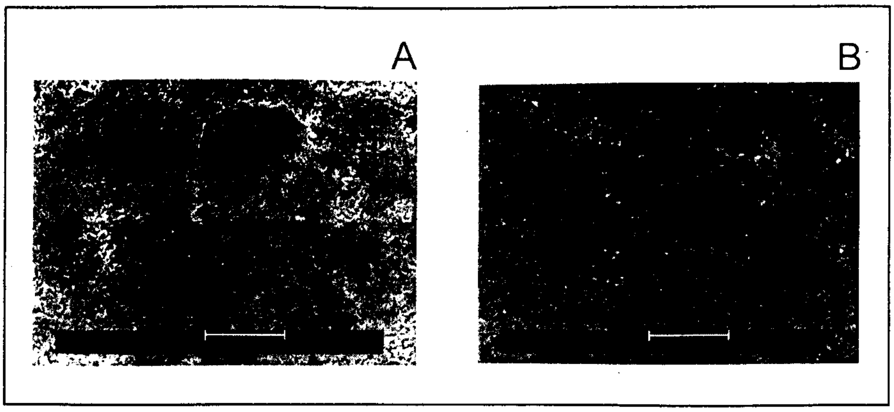

Fig. 7. Surface SEM micrographs of DST papers, coated with 100 pph GCC + 20 pph latex 51-H and fixed at (A) 30 m/min with 20 kN/m or at (B) 30 m/min with 50 kN/m. Scale bars = 20 μm.

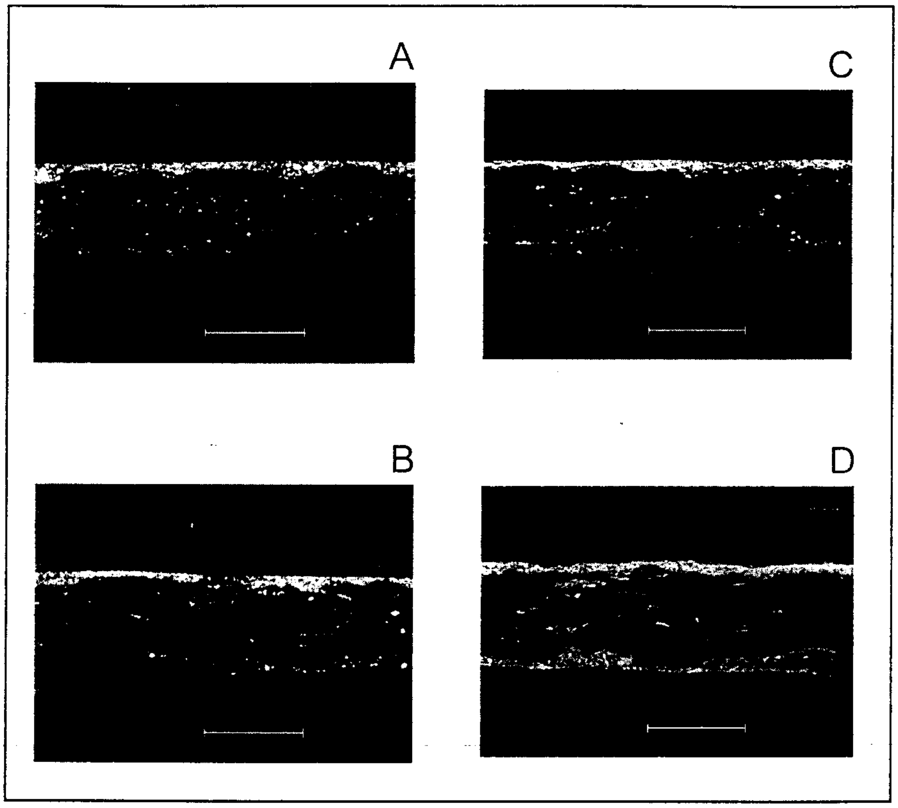

Fig. 8. Cross-section SEM micrographs of DST papers, coated with (A) 100 pph GCC + 10 pph latex 51-H, (B) 100 pph GCC + 10 pph latex 20-H, and (C) 100 pph GCC + 10 pph latex 45-M, fixed at 10 m/min with 50 kN/m, and (D) the reference paper. Scale bars = 50 μm.

stronger aggregation of particles, especially with the low-T_g binder, caused more pronounced coating nonuniformities. With the high-T_g binders, the layer appeared relatively uniform, although rough compared to coatings with a lower binder content. In some regions, the higher roughness was clearly due to the sticking deposits, the formation of which was especially enhanced with latex 45-M (Fig. 9B).

Judging from the micrographs, penetration of the coating into the surface pores of the paper appeared to be more pronounced in the case of the wet-coated reference than for the DST papers. Extraction of the fibres enabled a visual examination of the reverse side of the coating. A rough coating reverse-side topography is likely to correlate with a higher degree of coating penetration, which might promote mechanical interlocking between the coating and the substrate and thereby contribute to the surface strength of the coated paper. The SEM micrographs of the reverse side of DST coatings containing 10 pph binder indicated a low roughness, although the roughness seemed to increase with a higher deformability of the binder, i.e. with a lower T_g and a lower gel content of the binder and especially when fixed with a higher linear load. At a binder content of 20 pph, there were no significant differences in the coating reverse-side topography observed between coatings containing latexes 45-M and those containing 51-H (Fig. 10), but coatings containing latex 20-H were too aggregated to distinguish the roughness caused by fibres in contact. The fibre impressions in the reverse side of the reference coating appeared somewhat less defined, probably due to a higher variation in the coat weight and a significant degree of interlocking.

At a higher magnification, the DST coating/paper interphase appeared to be smoother and have a lower degree of penetration into the paper surface when compared to the reference (Fig. 11). However, the binder, in this case latex 51-H, clearly had formed a film and a number of interlocking arms into the fibrous surface, although a more porous structure of the reverse side of the DST coating is evident.

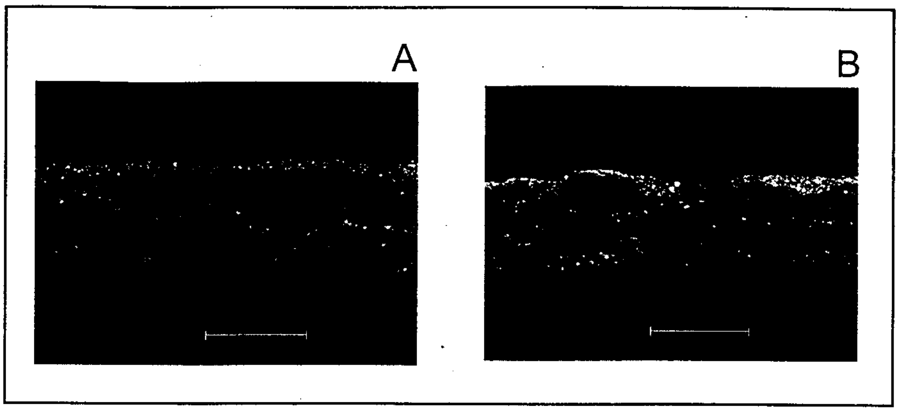

Fig. 9. Cross-section SEM micrographs of DST papers, coated with (A) 100 pph GCC + 20 pph latex 51-H and (B) 100 pph GCC + 20 pph latex 45-M, fixed at 30 m/min with 20 kN/m. Scale bars = 50 μm.

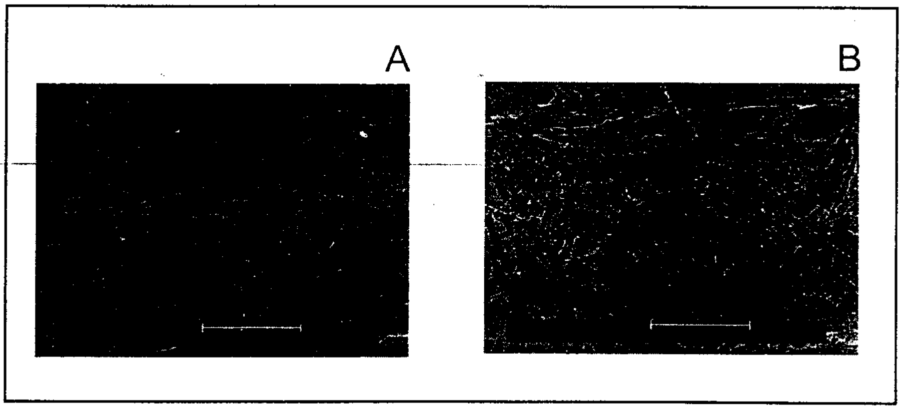

Fig. 10. SEM micrographs of the reverse side of (A) a DST coating, coated with 100 pph GCC + 20 pph latex 51-H, fixed at 30 m/min with 50 kN/m, and (B) of the reference coating. Scale bars = 500 μm.

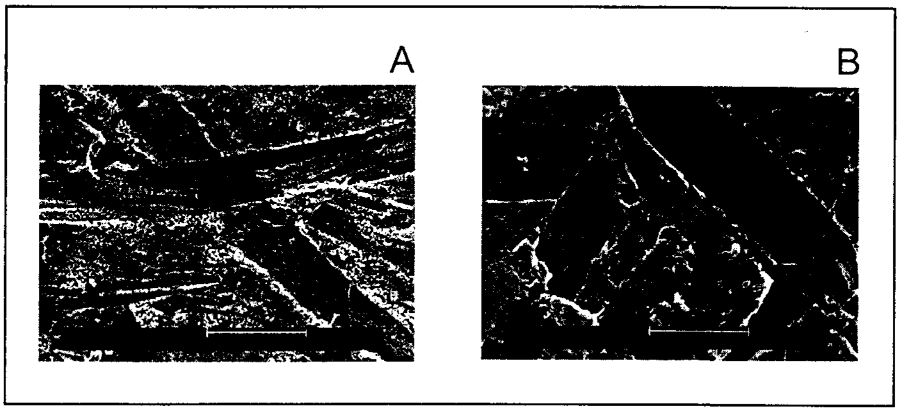

Fig. 11. SEM micrographs of the reverse side of (A) a DST coating, coated with 100 pph GCC + 20 pph latex 51-H, fixed at 30 m/min with 50 kN/m, and of (B) the reference coating. Scale bars = 50 μm.

Paper Characteristics

The average pore size (diameter) of the DST coatings was in the 0.2–0.5 μm range irrespective of the coating composition and fixing parameters and thus relatively large compared to that of the typical wet-coated papers [17,18] and the reference paper used here (Fig. 12). The porosity or the void volume of the coated papers was determined to be in the pore size range 0.02–0.5 μm. At a binder content of 10 pph, the porosity was 15–50%, where the lowest values were obtained under the shorter dwell time and the higher linear load. The densifying effect, and thus the lower porosity in the 0.1–0.2 μm range of the higher binder content (20 pph) was observed with all binder types. At a binder content of 20 pph, the coating porosity was 10–40%, where the lower gel content latex 45-M produced a slightly more compacted structure in the pore size range ~0.1 μm than the higher gel content latexes. Nevertheless, the dominating void size remained large.

The porosity was found to correlate with the fixing conditions. A longer nip dwell time produced a slightly finer pore structure, smaller dominating pore diameter, and a higher linear load resulted in a lower porosity.

The effect of the thermal post-treatment on the pore structure was small. The average pore size remained rather large and, in contrast to the expected effects, the porosity increased slightly.

The coating pore structure of the DST papers was reflected in their air-permeability and oil-absorption properties, as well as in the surface strength. The Bendtsen air permeability and the steady-rate oil absorption coefficient of the various coated papers are compared in Fig. 13 at a binder content of 20 pph. A higher value of oil-absorption coefficient indicates a more open (absorbing) inner structure of the coating layer. The relation between the void volume and the IGT surface strength at a different coating composition and fixing conditions is shown in Fig. 14. The binder content was 20 pph.

The reference value for the Bendtsen air permeability was 6 ± 1 mL/min and for the oil-absorption coefficient 3.0 $\text{mL/(m}^2\cdot\text{s}^{0.5})$, and the corresponding values for DST papers were relatively high. Note also that the reference was coated two sides, while the DST papers were treated on one side only. Although the influence of the coating composition and the fixing conditions was not very marked for either of the properties, there was a tendency for both of them to be influenced more by the pore size than the porosity. The oil-absorption coefficient, as well as the air permeability, attained lower values at the longer dwell time in the nip, i.e. for coating layers with a lower average pore size. Note here also the more open structure of the coatings containing the high gel-content latex 51-H [2]. The binder content had only a rather small effect on the air permeability. The same applied to the oil-absorption coefficient of coatings, although somewhat lower values were noted at the lower binder content 10 pph. A higher oil- absorption capability of the coating at a higher binder content could be related perhaps to an affinity between the oil and the binder itself [19], but the contribution of the binder was not confirmed here. A more uniform sealing of the paper at a binder content of 10 pph can also be attributed possibly to the smaller average size of the coating particles containing a lower amount of binder.

The surface roughness volume or the initial fast uptake of oil indicated rather equivalent surface-absorption properties of the DST papers at binder contents of 10 and 20 pph. The reference paper had a surface roughness volume of 3.7 mL/m^2. For DST papers with a binder content of 20 pph, the values ranged between 3.1 and 5.2 mL/m^2 and decreased with increasing linear load in the fixing phase. Comparison between the binders showed that the surface openness was enhanced with the low-T_g latex 20-H, again presumably due to the aggregated character of the coating layer.

The reference value for porosity was

33% and the reference paper did not exhibit any failure of the surface strength at the IGT test conditions chosen. The DST coatings with 20 pph latex 45-M showed excessive sticking at the lower fixing speed, causing rupture of the coating layer, and they were not included in the tests. Throughout this coating series, it was noted that increased speed during the fixing stage could reduce the sticking tendency. On the other hand, an increased speed combined with an insufficient heating of the coating layer could promote cohesional failure of the coating layer.

In general, at a binder content of 20 pph, the latex 51-H produced a rather satisfactory picking resistance of the DST papers in the IGT tests. There was no coating rupture observed in most of the cases (Fig. 14). A sufficient surface strength (no coating rupture at the chosen test conditions) was noted also with coatings containing 20 pph latex 45-M when fixed at the higher velocity. With the high-T_g latexes, an improved surface strength was usually related to a low porosity (Fig. 14) and low surface roughness volume at both binder contents. However, although the expected relationship between the fixing conditions and porosity was found also for coatings containing 20 pph latex 20-H, those DST papers exhibited an insufficient picking resistance. This is to be attributed to particle aggregation, perhaps combined with an insufficient deformation during the fixing phase, thus leaving a smaller contact area for adhesion to the paper surface. Typically soft film-forming latexes are expected to give an improved binding power and thereby to reduce coating dusting or failure [15]. In this study, the aggregation of the coating particles seemed to overshadow the possible advantages of a low-T_g binder.

The reference paper had a PPS-s10 surface roughness of 2.8 μm. The surface roughness of the DST papers ranged between 1.2 and 2.0 μm for coatings containing 10 pph latex and between 1.5 and 2.0 μm with 20 pph latex, the lowest values in both cases obtained with coatings containing latex 51-H and fixed at the lower speed and the higher linear load. This, combined with the results from the oil-absorption experiments, indicated, in a sense, that the surface of the DST papers was smooth and relatively dense, but the internal structure of the coating layer should be more compacted to compare more favourably with the mechanical cohesion and absorption properties of the conventional wet-coated papers. Thus, it is interesting that, although the coating containing a latex with a high T_g and a high gel content had a more open coating structure, reduced sticking tendency and improved surface strength were achieved with this latex. This may open up possibilities in improving the mechanical performance of DST coatings, even at low binder levels.

Ink Interactions with the Paper Surface

Some of the DST papers were tested also for their interaction with ink using an ISIT tester. We found relatively small variations in the ink setting behaviour associated with various coating compositions and fixing conditions. Therefore, we describe only some general observations from the ISIT tests. In general, DST papers exhibited a slower ink setting ability and lower tack peak values than the reference (Fig. 15).

Donigian et al. [20] and Zang et al. [21] concluded that a coating with a fine pore size was more effective than a coarse structure at pulling the ink solvent from the setting ink film, resulting in a fast tacking of ink. By applying the concept of preferred pathway of pore-filling fluids [22], the initial tack rise of ink can be attributed to the volume and connectivity of very fine sized pores, which are effective in fast absorption of the low-viscosity portion of the ink vehicle. Similarly, a higher tack peak value and a faster decay of the surface tack reflects a high available pore volume of appropriate-sized

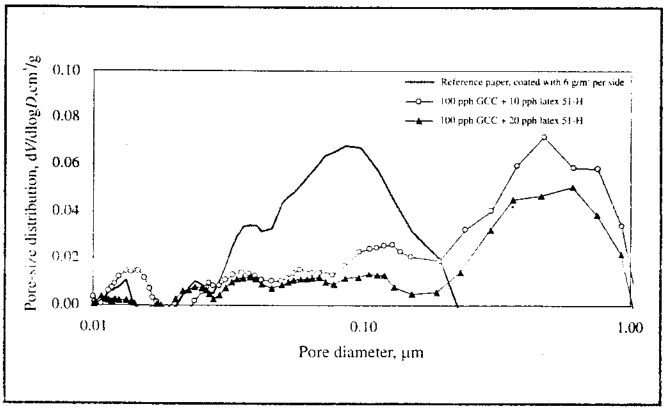

Fig. 12. Coating pore-size distribution of DST papers coated with 100 pph GCC + 10 pph latex 51-H or 100 pph GCC + 20 pph latex 51-H, fixed at 30 m/min with 20 kN/m, and the reference paper.

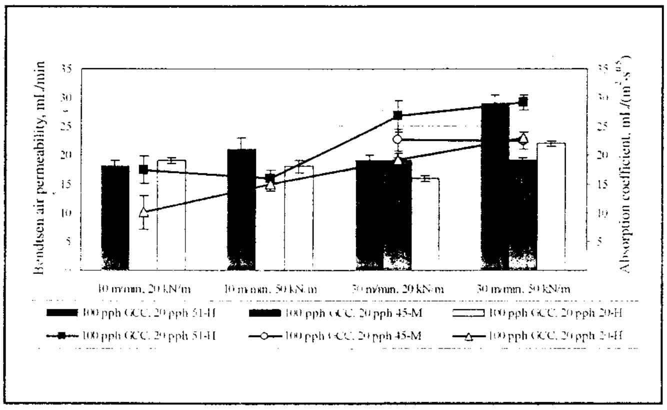

Fig. 13. Bendtsen air permeability (columns) and absorption coefficient (symbols) of the DST papers coated with 100 pph GCC + 20 pph latex, fixed at varying speeds and linear loads.

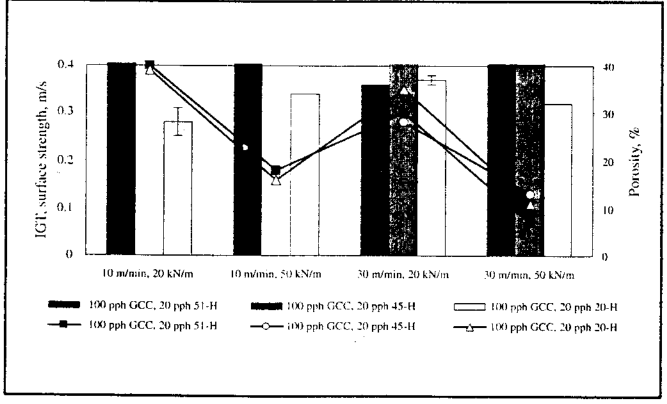

Fig. 14. IGT surface strength (columns) and porosity (symbols) of DST papers coated with 100 pph GCC + 20 pph latex, fixed at different speeds and linear loads.

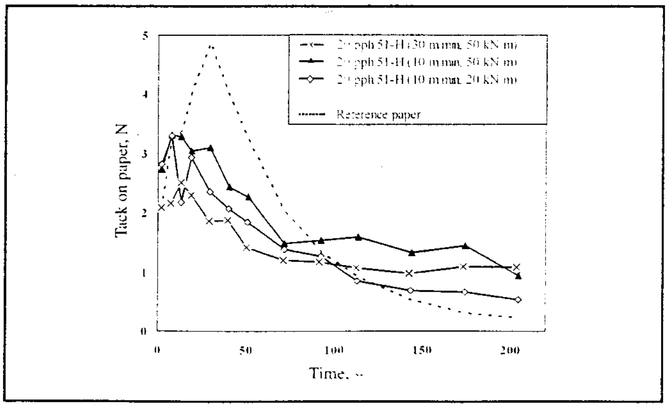

Fig. 15. Ink tack curves for three DST papers coated with 100 pph GCC + 20 pph latex 51-H and fixed under various conditions, and for the reference paper.

pores.

The moderate tack decay on DST coatings correlated with the results obtained of the pore structure; the powder-formed coatings contained a small amount of fine pores. The tack buildup time was longer for DST papers fixed at the higher linear load, i.e. with a lower porosity, which as such is in accordance with observations made in [20]. A comparison of the DST coatings in Fig. 15 revealed that the one fixed under a longer dwell time and a lower linear load had a dominating pore size of ~0.3 µm and a porosity value of 41% and thus exhibited a faster setting of ink than that of a coating fixed under a higher linear load and with a dominating pore size of ~0.2 µm and a porosity of 18%. The coating fixed under a shorter dwell time and a higher linear load had a dominating pore size of 0.6 µm and a porosity of 7%. In this case, the very large size of the pores may have affected the ink setting capability, as already indicated by the high air-permeability and oil-absorption properties of this paper.

CONCLUSIONS

The surface structure and performance of DST papers depend, as expected, on the coating composition and fixing conditions. Here, improved coating uniformity and surface strength of DST papers required smaller particle (aggregate) sizes and a polymeric binder with a high or at least a medium-high gel content to avoid the coating sticking to the heated roll surface.

Compared to conventionally wet coated papers, the DST coatings had a lower penetration into the pores of the paper surface, indicating a lower capability for mechanical interlocking. An increased binder content increased the interactions between the coating and the paper, but could impair the performance by a too-strong sealing of the coating layer.

The average pore size of DST coatings was larger than that of the conventionally coated papers and the porosity of the DST coating layers was in many cases quite high. On a submicron scale, the openness of the structure was reduced with a higher binder content, with binders having a higher deformability and with increased linear load in the fixing phase. On the other hand, on a larger scale, the surface homogeneity suffered from aggregation caused by a higher binder content.

The openness of the coating structure of the DST papers resulted in higher air permeability and oil absorption than the wet-coated reference paper. However, the surface smoothness and the surface roughness volume of the papers were comparable.

Preliminary experiments indicated that the DST papers exhibited a slower setting of ink than the suspension-coated and soft-calendered reference paper.

An optimal combination of the thermomechanical properties of the binder and the fixing conditions should be found to give porous but mechanically resistant coating layers at low binder contents. A challenge in the preparation of DST coating particles is to combine the improved film-forming properties of a low-T_g binder with a fine particle size.

Although the coating containing a latex with a high T_g and a high gel content had a more open structure, reduced sticking tendency and improved surface strength of the DST papers were achieved with this latex. This may open up possibilities in improving the mechanical performance, even at low binder levels.

ACKNOWLEDGEMENTS

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KEYWORDS: COATING COLOR, DEPOSITION, SURFACE TREATMENT, DRY PROCESS, BINDERS, ELASTICITY, MECHANICAL PROPERTIES, THERMAL PROPERTIES.

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A comparison of LWC papers produced using blade and MSP coaters

The use of the metered size press (MSP) for coating is on the increase, especially for LWC offset papers, where it now accounts for nearly one third of European production.

A single on-line MSP coating station exerts less stress on the base paper compared to a blade coater, thus allowing the use of more recycled fibre or filler. High machine speeds can also be achieved, thus making the MSP a cost-effective method of coating.

It has been shown that both blade and MSP coaters can produce good quality paper. However, the application method can have a significant effect on the coating structure and this means that MSP coated papers tend to have a different balance of paper and print properties.

In a kaolin-rich formulation, the MSP coater was found to produce a sheet with slightly lower sheet gloss and greater roughness. However, the MSP coater also gave improved fibre coverage (contour coating rather than void filling) that would result in more even printing properties.

Commercial LWC papers are made commercially, they have to exhibit a minimum paper quality level and acceptable print runnability. Therefore, paper makers have tended to reduce the quality differences that could occur between the coater

In the late 1980's, the development of MSP process enabled the surface coating of paper products to slightly upgrade the print quality of an uncoated woodfree paper, or to provide a precoated layer. In the 1990s, the process was improved with the advent of larger metering rods, and in 1993, M-real Kirkniemi produced the first coated paper, as opposed to a lightly pigmented paper, which became the Galerie Lite brand.

In recent years, MSP coating has increased considerably, due to the success of this paper grade and the economic advantages associated with the technology. Currently approximately 35% of HSWO LWC mechanical papers are produced using MSP coating technology, *Figure 1*.

Recent developments have been the introduction of very high-speed machines, for example by Cartiere Burgo and Haindl Augsburg(1). If the reader requires more general information on metered size press coating, the papers and references from the three previous TAPPI Metered Size Press Forums are an excellent starting point(2,3,4).

The MSP coater represents a lower investment cost than blade coaters, as both sides of the paper can be coated at only one station. This also makes it easier to upgrade older and slower machines. Producers of double or triple coated mechanical papers can apply the first coating layer on-machine to improve efficiency.

Other advantages include a productivity gain over blade coating due to faster running speeds (up to and over 2000 $m.min^{-1}$), less web breaks than a blade coater, and use of either a lower basis weight or weaker base paper.

This feature analyses the differences in coating structure and print quality resulting from a single kaolin colour being applied to a basepaper with two different types of applicator. The offset print quality is also assessed.

In the second part of the feature, a number of commercial papers are assessed, to determine whether these differences in paper and print performance still exist after optimisation of the coating and basepaper for that coater type by each paper maker.

Experimental Materials

In the first part of this analysis, a single coating colour was applied to the same basepaper with the two different applicator types.

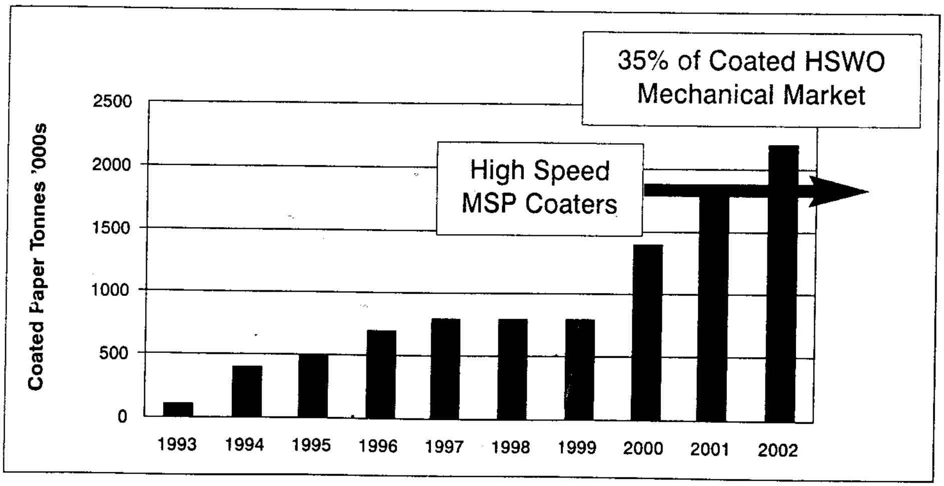

Figure 1. Growth of MSP coaters between 1993 and 2002 in European coated mechanical paper (from O'Neill(1))

types by optimising both the basepaper and coating formulation for each application technology.

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The same coating was applied to a 41 gm^{-2} newsprint basepaper using both a Valmet Autoblade (trailing blade coater) and a Valmet Symsizer (MSP coater).

The formulation consisted of 100% English kaolin, 10 pph Dow 955 SBR latex, 1 pph FF5 CMC and 0.5 pph C104 lubricant. The colour solids was 58-59 w/w%. and 10 gm^{-2} of coating was applied to each side of the paper, at a coater speed of 900 m/min. The coated papers were supercalendered at 100°C, 400 m/min and 300 kN/m pressure.

These coatings were analysed for differences in paper quality, coating structure and offset printability.

In the second part of this study, a range of LWC papers were obtained from different paper mills for evaluation. These papers were either 48 gm^{-2} or 60 gm^{-2} and were coated using either a MSP or blade coater. These papers were compared in a benchmarking study to determine any differences in their coating structure and printability.

Test Methods

The papers were allowed to condition at 50% relative humidity and 23°C for at least 24 hours before standard laboratory paper testing was performed (TAPPI 75° gloss on Hunterlab; ISO brightness and DIN opacity on Elrepho 3300; PPS at 1000 kPa on PrintSurf).

The alignment of kaolin particles parallel to the surface can be determined using X-ray diffraction(5,6,7). For kaolin, an alignment index can be defined by a, where a low value for a indicates a well-aligned kaolin coating.

SEM microscopy was used to determine the thickness and coating structure of the surface layers of the coatings. The mineral content of the papers was assessed using the EDX attachment on the SEM microscope.

This method gives an estimation of the proportions of minerals present in the coating layer by comparison of the ka peak heights from the kaolin (Si) or calcium carbonate (Ca) peaks. By comparing the peak heights Si/(Si+Ca), with a calibration chart, the % kaolin in the coating can be estimated.

Mercury intrusion porosimetry (using a PASCAL 240 Porosimeter, CE Instruments) was used to determine the average pore size of the coating layers. Curve fitting programmes were used to subtract data for the coating from those of the basepaper. This is described in more detail in reference(8).

The papers were printed using a commercial magenta sheet fed ink. The thickness of ink applied to the coating was approximately 1 μm in every case, which corresponds to a volume of 0.3 cm^3 applied to the inking rollers. Ink films were applied to the coated paper strips using a commercial laboratory printing unit (AC2, IGT).

The inked printing disk was attached to the lower printing unit and the substrate printed at a pressure of 500 N and a speed of 0.5 ms^{-1}. The print density was measured using a Gretag Macbeth densitometer (D186 Zurich)(9), and the Tappi gloss of the prints was assessed at an angle of 75°.

The ink setting behaviour was studied by following the development of the ink tack force using the Ink Surface Interaction Tester (ISIT), (SeyGan Ltd, Lostwithiel, UK). The principle is described by Gane and Seyler(10). The instrument measures the force required to separate a trilayer consisting of the paper surface, the ink layer, and the rubber printing blanket. The failure takes place at the weakest point which will change with time as the ink dries. The initial part of the ink tack curve is related to the rapid imbibition of the ink solvents into the coating, which is related to the porosity characteristics of the coating layer(8). In this work the ISIT results are quoted as a time to reach the maximum tack force.

Results: MSP vs. Blade (kaolin coated paper)

The coated paper and printing properties are shown in *Table 1*.

The optical properties of the coating layers do not differ significantly, *Table 1*. The blade coated paper has a slightly higher sheet gloss and is also smoother than the MSP coated paper. This is consistent with the view of the blade coater producing a void filling action and also aligning the kaolin particles parallel to the paper surface.

	Blade	MSP
Paper coating properties		
Gloss / %	54	52
Brightness (ISO)	74.1	74.1
Paper substance / gm^{-2}	62.5	62.1
Paper caliper / μm	53	52
Paper density / g cm^{-3}	1.49	1.47
Opacity (DIN)	90.8	90.9
PPS 1000 kPa	1.2 μm	1.5 μm
Printing results		
Print gloss / %	81	74
Print snap	27	22
Print density	1.49	1.47
ISIT™ Time to Maximum Tack Force / s	50	50
Wet pick resistance	0.7 cm/s	0.5 cm/s

Table 1: Paper and print properties of coating applied by 2 different applicators

This particle alignment can be seen in *Figure 2* where for both uncalendered and calendered samples, the blade coating has superior particle alignment compared to the MSP coated paper.

It can be seen that in general, the MSP coater has produced paper with more even coverage and less void filling, with a slightly narrower coating thickness distribution, *Figure 3*. This is generally accepted to be the case, as the relatively low pressure in the MSP coater application nip does not force the coating colour into the surface pores of the basepaper. However this slight difference in coverage has not altered the density of the coating layer to any significant extent.

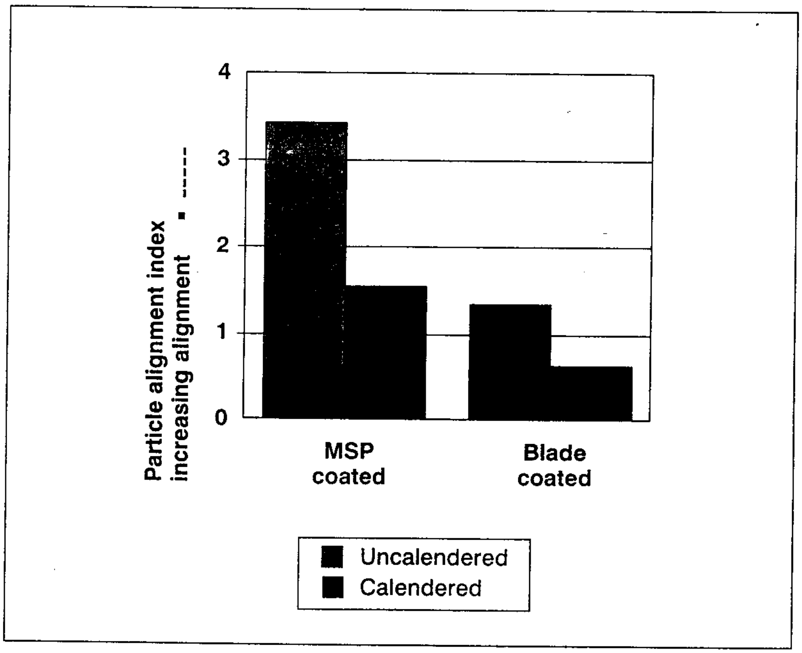


Figure 2: XRD particle alignment MSP and blade coated paper, showing increased particle alignment for blade coating

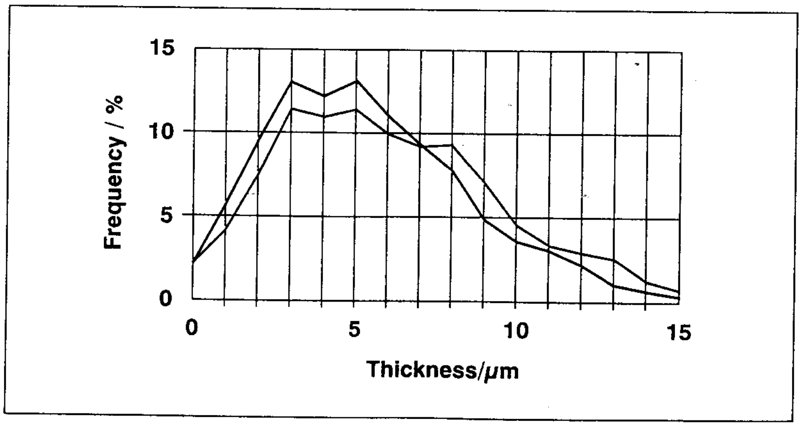


Figure 3: Coating thickness distribution for blade and MSP coated papers showing, a narrower distribution (better coverage) for the MSP paper

The print snap – difference between print gloss and paper gloss – as seen in *Table 1*, is lower for the MSP coating than the blade coated paper. This trend is often as a result of differences in the ink setting rate of coated surfaces, with faster ink setting papers not allowing the ink to level to any great extent before ink film consolidation(8).

The prints may also have an increased micro-roughness due to a depletion of ink resin at the surface of the print leaving the ink pigment particles protruding from the ink film surface(8). As the ink tack rise times are the same, *Table 1*, the latter mechanism is likely to be more important in this case.

A previous study(11), which looked at variations in particle alignment and ink setting rate with changes in calendering conditions, also found no difference in ink tack rise time between an uncalendered coating with poorly aligned kaolin particles and a highly calendered paper. This suggests that the difference in the size and number of pores at the surface of the coating layer are quite similar, as these parameters have been found to influence the removal of oils from the ink film, which in turn controls the ink tack rise time(8).

The wet pick results indicate that the MSP coated paper is slightly weaker than the blade coated paper. It was observed that the picking occurred at the coating/base interface and not in the coating layer. This could be due to less binder being lost into the basepaper as a result of the lower pressure exerted on the coating during coating when using the MSP.

In this trial the MSP coater has produced a sheet where the coverage of the basepaper is only slightly better and a more contour coating layer has been formed.

This combination of effects has produced a rougher sheet with slightly lower sheet gloss. The difference in kaolin particle alignment data seems to indicate that the structure of the MSP coated paper is more disordered compared to the blade coated paper, but there is little evidence for this in the optical data, with similar paper brightness and opacity levels. This lack of difference in the optical properties of the coatings may lie in the fact that there is little real difference in the pore volume of the coating layers. Greater light scattering requires greater pore volume (at the right pore size).

The particle alignment for the MSP coated paper will always be worse than the blade coated paper, even if all of the kaolin particles lie parallel to the surface. The contour-coating nature of the MSP coater ensures that the overall coated paper roughness is greater and the particles are less well-aligned relative to a flat plane. This is shown schematically in *Figure 4*.

The identical paper density and bulk measurements as shown in *Table 1* would also support this theory. However, other data exists(12) showing that when blends of a blocky calcium carbonate and a platey clay are used, there may be differences in coating layer disruption and light scattering, as a result of different coating applicators.

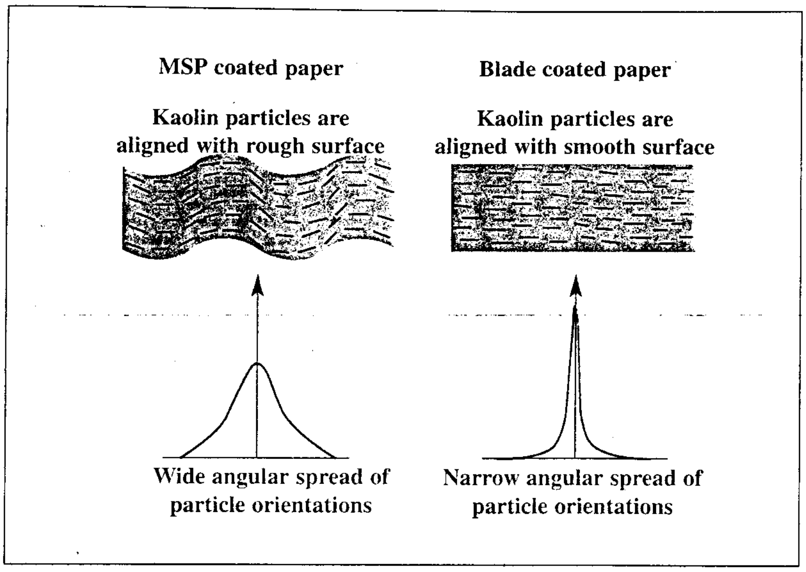


Figure 4: Schematic diagram of kaolin particle alignment for MSP and blade coated papers

The printability results show that the MSP coater has produced a lower print gloss and print snap. The print density is also slightly lower, indicating that slightly less ink has transferred to the coating from the printing blanket. The ink tack rise times are the same for both coatings.

Benchmarking commercial European MSP and Blade coated papers

The paper properties for the benchmarking study are shown in *Figures 5 to 14*.

In *Figure 5* it can be seen that the use of higher levels of kaolin in the coating generally produces papers with lower sheet density. This is probably due to the lower calendering requirements and higher glossing potential of kaolin compared to GCC.

The higher grammage papers tend to have higher ash levels than the lower grammage papers, as shown in *Figure 6*, but the MSP and blade coated sheets have similar ash levels.

In *Figure 7*, as expected, the higher grammage papers show greater sheet gloss levels. However, there is a small group of MSP coatings that have higher sheet density levels. It is possible that there is a higher level of filler in these papers, as the manufacturers take advantage of the lower strength requirements of the MSP coater. These papers also have a relatively low level of kaolin, *see Figure 5*.

As would be expected from the gloss results, the lower grammage papers tend to be rougher than the higher grammage ones, as

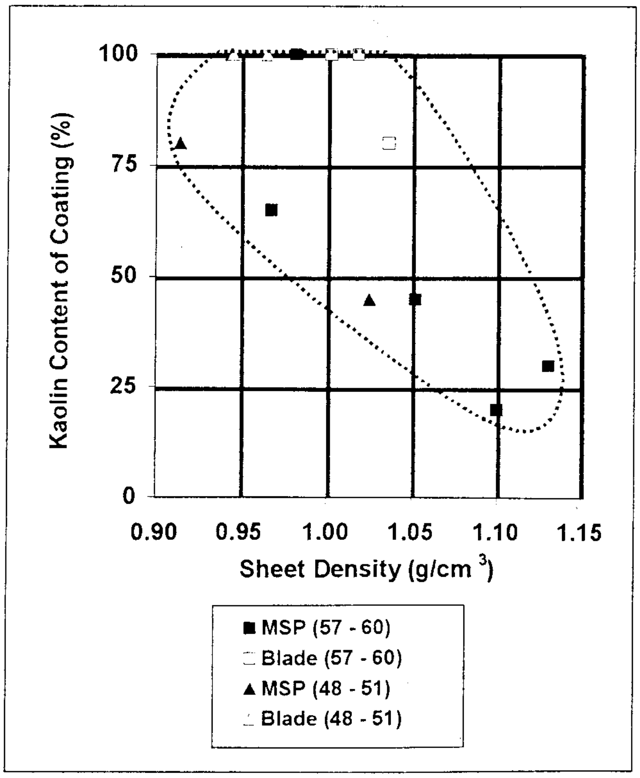


Figure 5: Effect of kaolin content in the coating on the sheet density

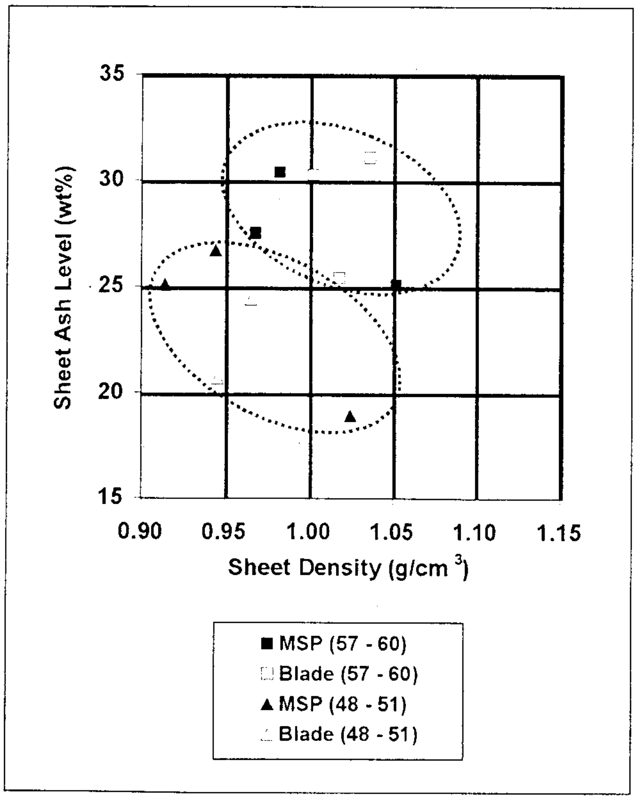


Figure 6: Effect of ash level on sheet density

shown in *Figure 8*. There is no evidence that the MSP coated sheets are rougher than those produced using a blade coater.

In *Figure 9*, the sheet gloss is plotted against smoothness. It is clear that the lower grammage papers have a lower gloss and a higher PPS than higher grammage papers. As expected, higher gloss is associated with smoother paper. However, within each grammage range there is no clear differentiation between the samples prepared using a MSP or blade coater.

The opacity and brightness of the coatings are shown in *Figure 10*. As expected, the

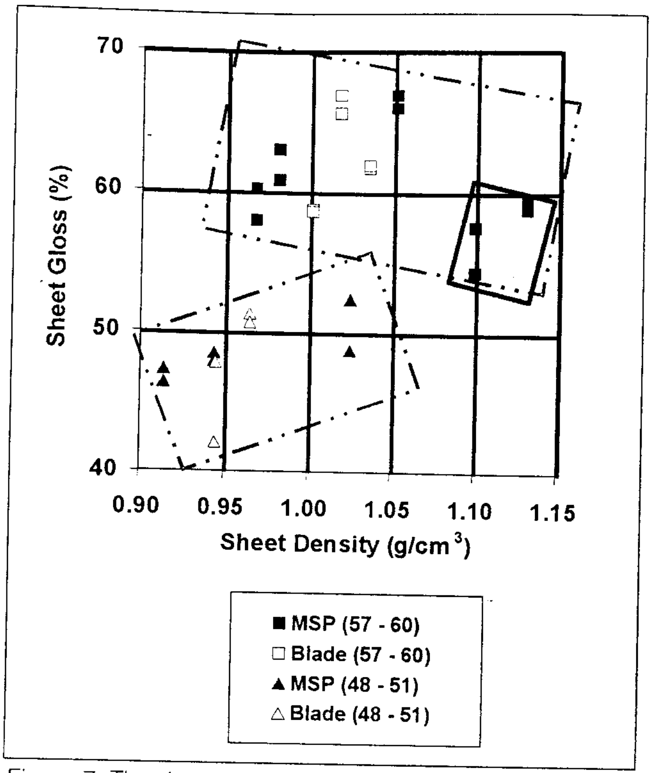


Figure 7: The dependence of sheet gloss on sheet density

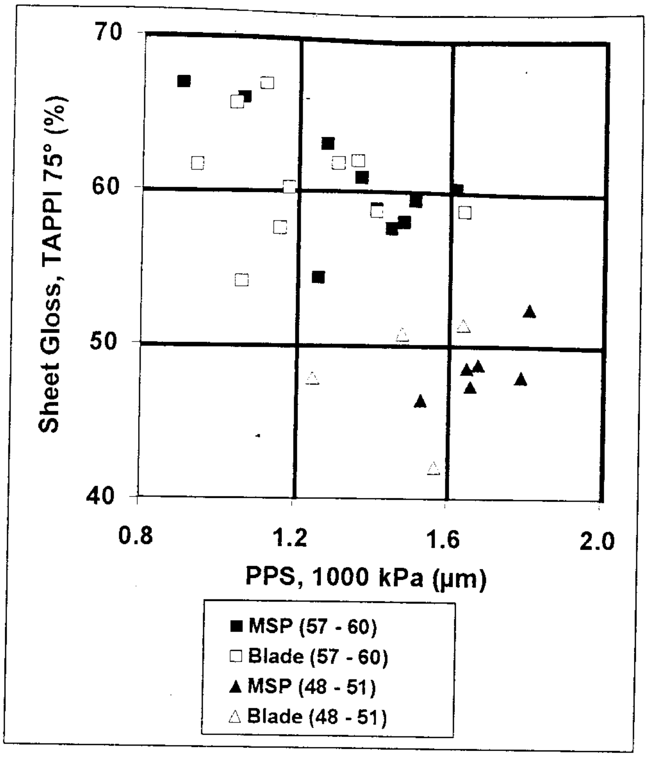


Figure 9: Relationship between sheet gloss and smoothness

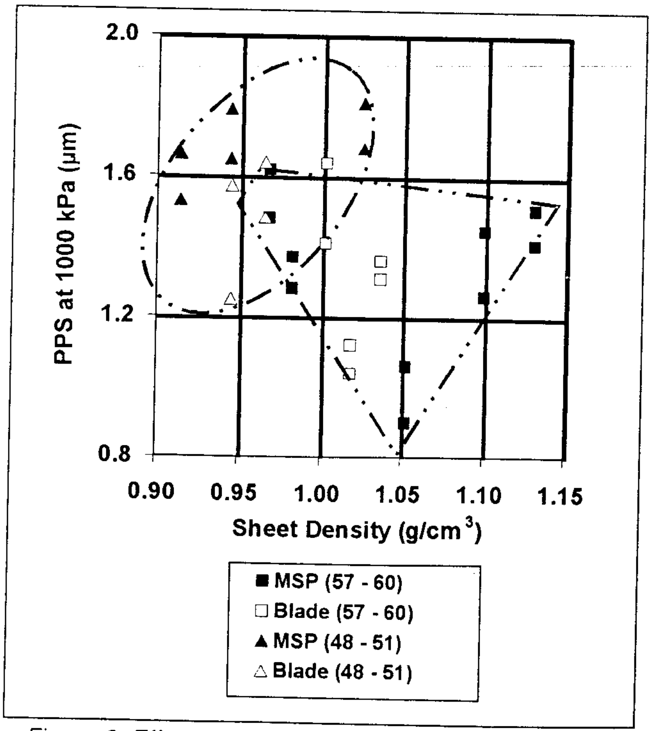


Figure 8: Effect of sheet density on paper smoothness

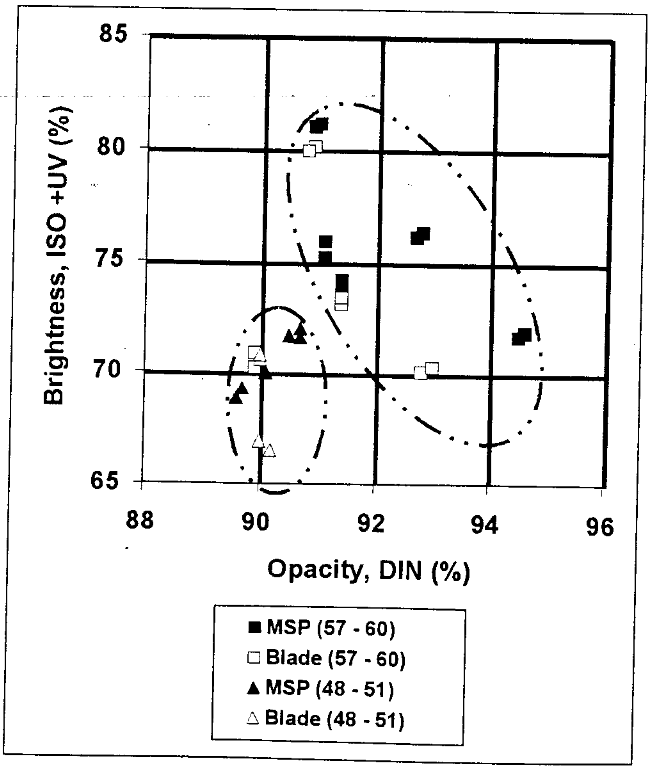


Figure 10: Relationship between sheet brightness and opacity

heavier grammage papers are giving both increased opacity and brightness. There is less variation in optical properties between the lighter grammage papers.

In *Figure 11*, it is shown that approximately half of the LWC papers show significant fluorescence, and of those that do, there is a mixture of blade and MSP coatings.

Surface micrographs

SEM micrographs of some of the coated paper surfaces have been included in *Figure 12*. In general, these reveal a more open surface for the MSP coatings, when looking at the higher grammage papers. However the lower grammage surfaces appear very similar.

Cross-sections of the coated papers were also studied in order to reveal any differences in the coating structure between MSP and blade coated papers. *Figure 13* shows a cross-section of one of the blade coated papers and one MSP coated paper at 48 gm^{-2}, which contain 100% kaolin. The slightly more open and disrupted nature of the pigment particles in the coating layer can be seen in the higher magnification cross-sections. However it is difficult to see any major differences in the coverage of the paper using the low magnification micrographs.

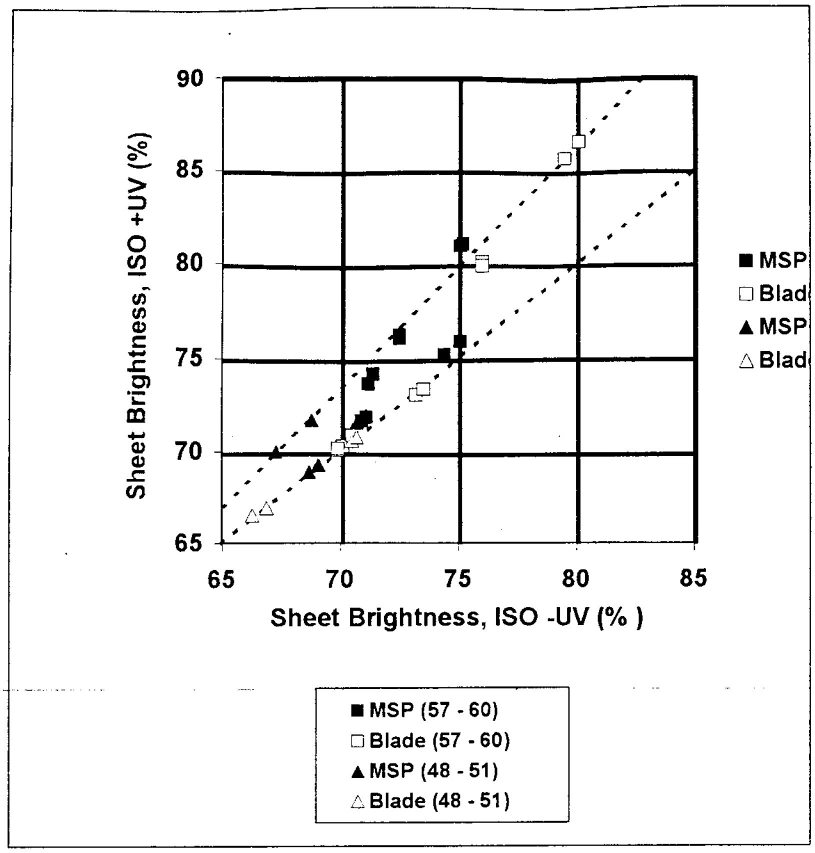
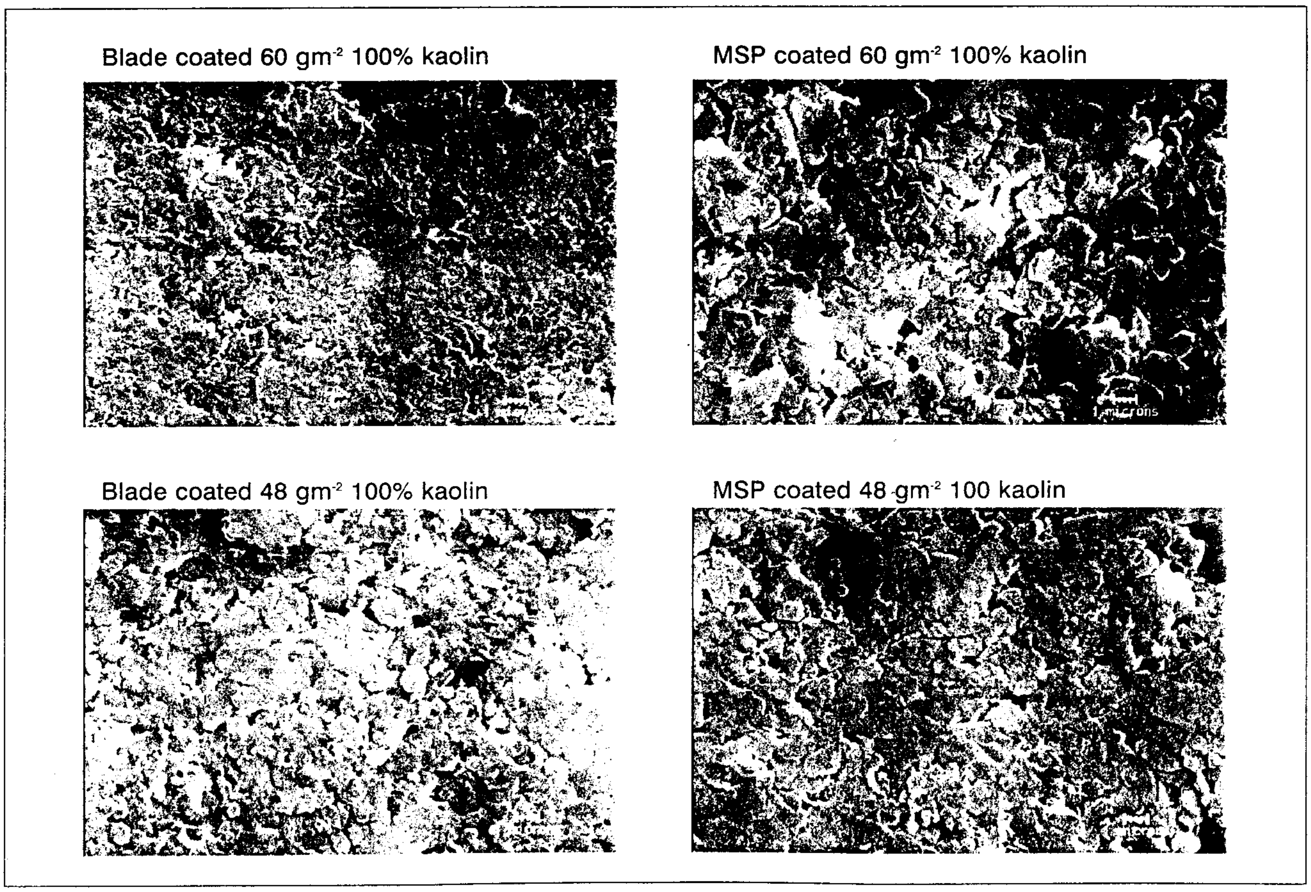


Figure 11: The relationship between sheet brightness with and without UV


Blade coated 60 gm^{-2} 100% kaolin

MSP coated 60 gm^{-2} 100% kaolin

Blade coated 48 gm^{-2} 100% kaolin

MSP coated 48 gm^{-2} 100 kaolin

Figure 12: Micrographs of coated papers at 2 different grammages

The mercury porosimetry results also confirm that in general the MSP coatings have a larger average pore size, as shown in *Figure 14*. However it should be noted that these differences are likely to be influenced by different carbonate levels in the formulation.

Offset Printability

The offset print testing results are included as *Figures 15-17*. In *Figure 15*, there is no obvious differentiation in print density between the MSP and blade coated papers, although there is more variation in the MSP coated samples.

There is a general trend of higher print gloss at higher sheet gloss, with little differentiation between the coating types, as shown in *Figure 16*. The papers with a lower grammage also have lower print and sheet gloss levels.

For some of the MSP coated papers, the initial ink tack development rate seems to be independent of the coating mean pore size, as shown in *Figure 17*. The MSP coated papers tend to have similar tack development but with larger pore sizes compared to those produced using a blade coater. This seems to confirm the observations made in the first part of this paper. Ink setting is controlled by both the size and number of pores per unit area in the coating.

This probably means that the MSP coatings have a lower number of larger pores compared to the blade coated sheets that have a higher number of smaller pores. These effects have been investigated in more detail[8]. The choice of pigment in the formulation is likely to be the dominating feature rather than the mode of colour application.

However, when looking at all of the printability results, it appears that there are no large differences in print quality between the MSP and blade coated papers. Indeed, it does appear that the papers have all been optimised to give acceptable print quality.

Conclusions

This work has shown that if the same kaolin coating colour is applied to a basepaper with a MSP applicator and a blade applicator, then there will be some characteristic differences in the resulting paper.

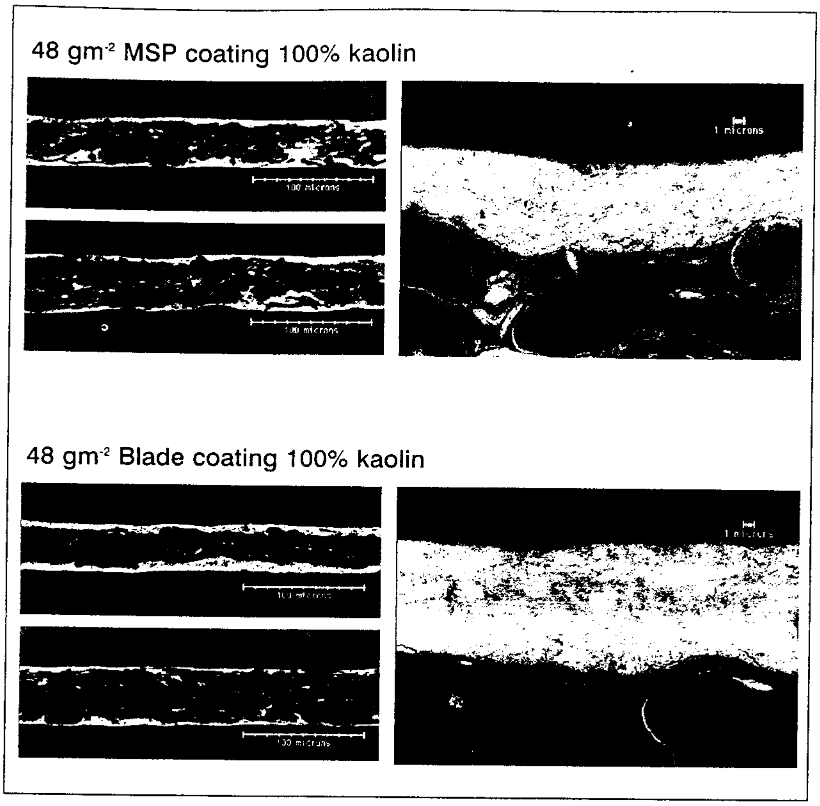


Figure 13: Cross sections of a MSP and blade coated paper

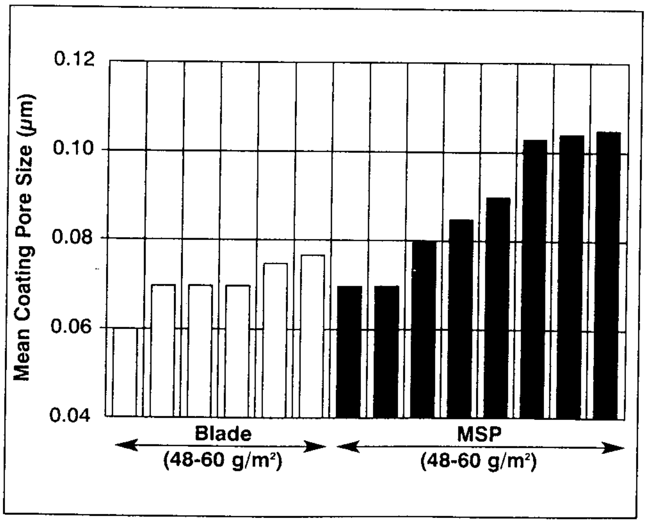


Figure 14: The mean pore size of the coating from mercury porosity measurements

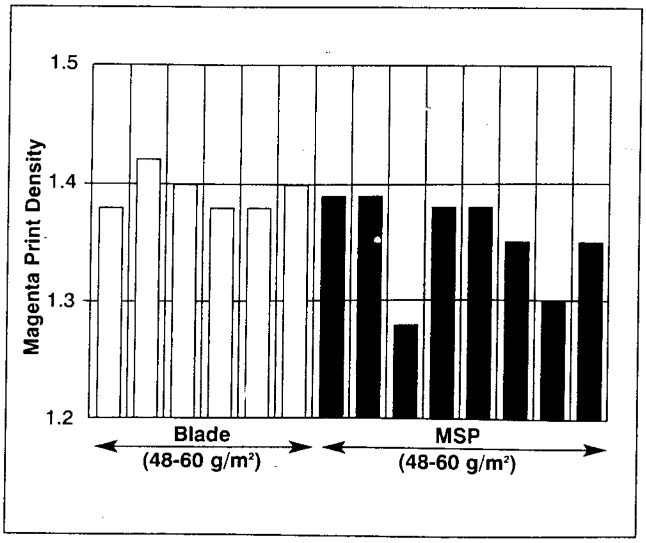


Figure 15: Offset print density

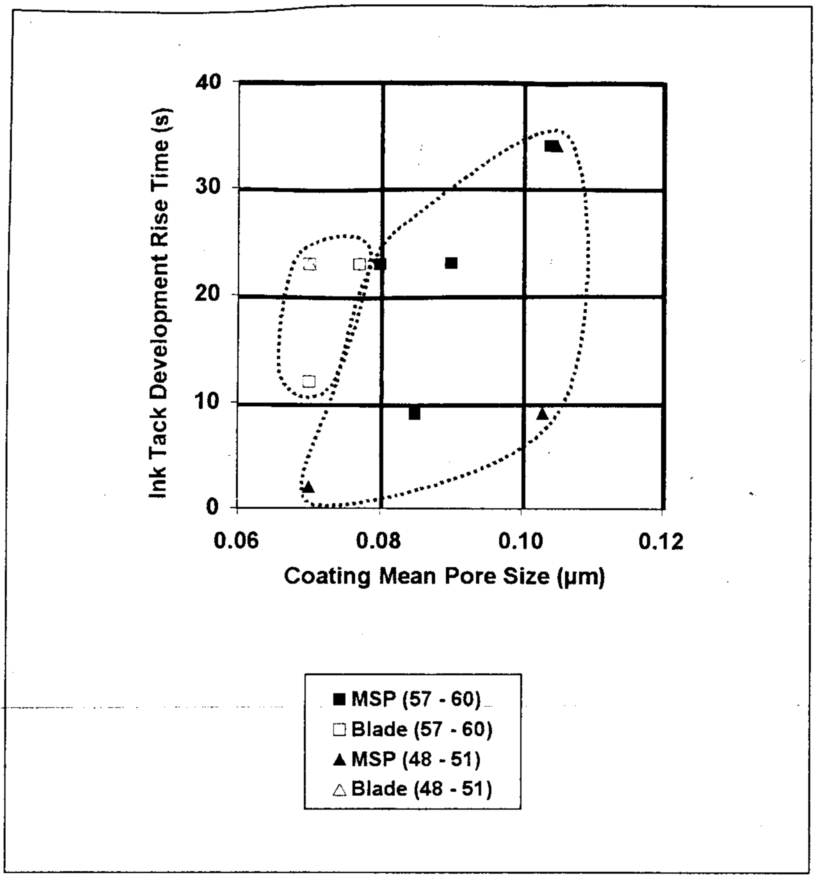


Figure 17: The dependence of ink tack development on coating mean pore size

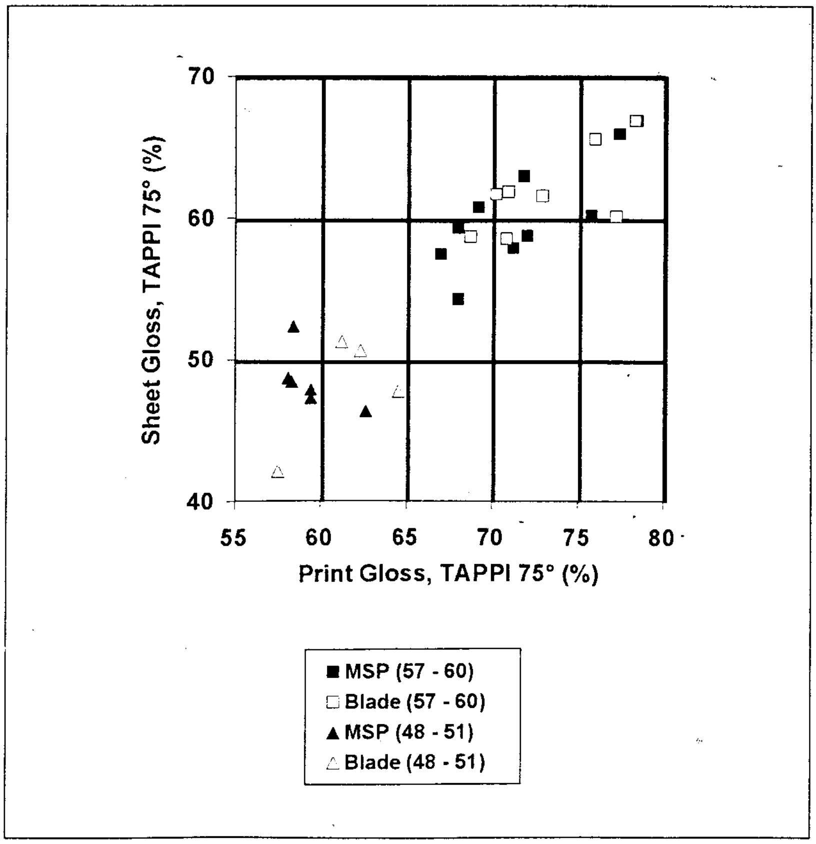


Figure 16: The relationship between print gloss and sheet gloss

The MSP coating will have slightly better coverage (contour coating rather than void filling), but will also be slightly rougher. There will be poorer alignment of the kaolin particles in the coating layer. This, together with the increase in roughness, will give a lower sheet gloss.

However, when looking at a wide range of commercially available papers at two different grammage ranges, it is evident that the papermakers have been able to trade off one property for another and they have effectively eliminated many of the differences arising from the use of different coater types. The papermaker can engineer the balance of paper and print properties both by optimising basepaper quality and the selection of coating pigments and other formulation components.

Pigment producers and papermakers have been working together for many years, to optimise paper and print quality, therefore it is not surprising that papers result which can compete effectively in the market place, whatever their method of production.

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