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EFFECT OF CLAY / LATEX RATIO ON HIDING POWER AND ABSORPTION CHARACTERISTICS OF COATED PAPERS

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ABSTRACT

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<u>Topic:</u> Effect of clay / latex ratio on hiding power and absorption characteristics of

coated papers, 50 pages (including references and 8 appendixes)

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This work presents a systematic study of the relationship between hiding power and absorption characteristics of clay-based coated. Commercial clay (SPS, English China Clays) was used as coating pigment with different ratio of binder (styrene-butadiene latex) to form coating colours for surface treatment of papers. With constant solids content (30% by volume), impacts of coated pigment with the

variance of binder's proportion (from 2 pph to 100 pph) were studied by investigating coated papers' properties: thickness, basic weight, and the optics (for white papers: remission curves, ISO brightness, and opacity; for brown papers: reflection coefficient R_o). Water penetration measurements were performed only for white papers. The water penetration tests yielded the penetration curves with theirs parameters (A – Cobb₆₀, W – wetting, and t – time till maximum).

All the results obtained for coated papers were compared with those of base papers, which allowed us to determine the usability of a given coating colour for certain kind of papers.

Key words: coating, surface treatment, printing papers, clay, latex, ratio of pigment and binder, water absorption, water penetration, and optical properties

1 INSTITUTE PRESENTATION

The project was done at the Institute of Papermaking and Printing at the Łódź University of Technology, Poland ^[1].

The academic and research activities of the Institute are realized by the following departments: Pulp Technology, Paper Technology and Paper Converting, Paper and Fibreboard Machines, Thermal Equipment and Converting Machines, Printing Technology and Machinery.

Interdisciplinary character of the Institute of Papermaking and Printing, the only institute of this kind in Poland (unique specializations: pulp and paper technology printing, paper packaging, paper engineering, papermaking, converting and printing machines), allows to carry out research projects from the initial idea through laboratory tests, equipment designed to testing a prototype for implementation in the industrial scale. Such projects can be easily done due to good material base of the Institute, including new laboratory equipment.

The Institute of Papermaking and Printing continues to develop contacts and cooperation with foreign universities, associations and companies, significantly contributing to upgrading teaching process and research development as well as allowing the students to gain new experiences, also abroad. All those activities and initiatives have a good impact on the future of the Institute of Papermaking and Printing – one of the largest education centres for papermakers and printers in Europe.

2 INTRODUCTION

Paper is an important medium for communication, education, artistic products, packaging, and sanitary and technical applications. In 2003, world production of paper and paperboard was 339Mt compared with 239 Mt in 1990. A split of this production for 2003 (table 1) indicates similar levels form North America, Europe, and Asia.

Table 1. Paper and paperboard production by region in 2003^[2]

Region	Production, kt	% of World Production (rounded up)
Asia	110.585	32
Europe	104.093	31
North America	100.280	30
Latin America	16.254	5
Australia	3.871	1
Africa	3.672	1
Total	338.755	100

Adapted from Paperloop 2004

Nonetheless, the paper industry finds itself facing new challenges with fierce competition and increasing raw materials and energy costs. In addition, the concern for environmental issues is growing. One way this has been achieved is through developments in technology which make the papermaking, coating and finishing operations much more efficient.

In paper coating, minerals are used as white pigments to conceal the fibre, thereby improving brightness, whiteness, opacity, and smoothness. Industrial minerals play a major part in the manufacture of modern paper, especially for coating process. Originally, because they were less expensive than fibre, minerals such as calcium carbonate and clay (kaolin) were used to reduce production costs. The coating layer is the top most layer of the paper and thus affects the surface properties of the paper. Most of the coating comprises of pigments and therefore by tailor-

making pigments, the surface properties of the paper can be fine-tuned. In this thesis, the study of effect of clay/latex ratio on hiding power and absorption characteristics of coated papers was presented.^[2.]

3 THEORY BACKGROUND

In the coating of paper, an aqueous suspension of coating colour is applied on paper. Generally, optical properties and quality of the coated paper are improved by filled cavities, covered fibres and smoothened paper surface. Moreover, one of the most important functions of paper coating is providing better printing in terms of print quality, image reproduction, printability and surface strength^[3]. Coating, however, decreases stiffness and ink absorption. After application the coating is dried and finished, usually by calendering to give paper the final smoothness and gloss. The coated papers in this thesis were prepared without calendering under laboratory scale.

The Scanning Electron Microscope (SEM) images of uncoated and coated paper surfaces are shown in figure 1. The first micrograph (1) of an 80 g/m² wood-free base paper clearly shows multiple layers of intersecting fibres. The paper surface is characterized by hills and dales formed by the fibre mesh. The voids between the fibres impair the smoothness and uniformity of the paper surface. The next micrograph (2) shows a pre-coated paper at the same magnification for comparison. A pre-coating of just 10 g/m² per side suffices to cover up the majority of voids and fibre crossings. This process helps smoothen and even out the paper surface. It is possible to enhance paper surface quality through application of a topcoat (micrograph 3). Coating the substrate with another 12 g/m² per side distinctly enhances the existing pre-coated surface quality even before the paper is calendered. At this stage, a number of dominant fibre structures and valleys still remain visible. Subsequent calendering further improves quality by enhancing

smoothness and gloss. The resulting surface is flat, with a minimum of irregularities (micrograph 4).

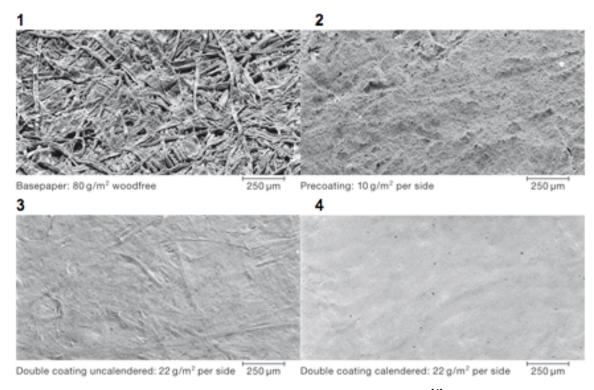


Figure 1. SEM of uncoated and coated papers with calender^[4]

Coating used in paper surfaces is a material composed by a complex mixture of components containing colloidal particles and dissolved polymers. Coating colour mixes consist of three basic components: pigments, binders, and water. The most important component is pigment, which in the dry coating is about 80-95 wt. %. The most common pigments in paper industry are clay and calcium carbonate with very small particles in which the size is less than 10 μ m. Another important component is binder. By definition, it helps to connect pigments and base paper. One or more binders are used in coating colour with the content of 5-20 wt. % of the amount of dry pigment. [5.]

3.1 Coating pigments

Pigment is the most abundant component in the coating since it presents 80-95 wt. % of the coating colour, so pigment is naturally the most important factor affecting the properties of the coating^[5]. High brightness and opacity are qualities needed for good pigments. The properties are based on effective light scattering of the material. Optimum size of a single round solid pigment particle for ultimate light scattering is a half of the wavelength of visible light (around 200 nm).

According to these properties and the economic issues, clay (kaolin) is the most common pigment used in the paper industry for coating. Clay is an inorganic coating pigment with its fine particle size, platy pseudo-hexagonal particle shape, good viscosity, low abrasion, good opacity, white colour, high brightness and good printability^[6, 7]. Kaolin is a type of rock formed through weathering or hydrothermal alteration of feldspar or mica minerals to clay mines, or sedimentary rock containing a high concentration of kaolinite particles or grains. Sedimentary kaolin rocks contain mostly clay or slit sized particles of kaolin minerals and fine and coarse particle size impurities. While the primary miner in kaolin is kaolinite, a hydrated aluminium silicate (Al₂Si₂O₅(OH)₄), kaolin also contains impurities. These impurities are undesirable in many industrial applications. Some of the impurities (e.g., fine ferruginous or titaniferous impurities) impact undesirable colour to the clay. [8.]

Clay has differences concerning morphological properties, chemical composition, and surface charge. The latter plays an important role for colloidal stability and dispersion constancy. Clay dispersion is the base of coating preparation, being the medium where the other formulation components are added^[9]. In aqueous medium the faces of the kaolin particles are always negatively charged while the edge has positive charge in acidic conditions and negative charge in alkaline conditions. When clay power is mixed with water and an anionic dispersing agent, the dispersing agent is adsorbed by the edges preventing agglomeration by electrostatic and steric hindrance and resulting in a stable dispersion. [10.]. One technique to change clay particle size and shape is mechanical delamination. This is the process of splitting apart kaolinite stacks or booklets into largely individual

platelets. One type of delamination operation involves subjecting the naturally occurring kaolin stacks to shearing forces in an extruder, thereby reducing the kaolin stacks to discrete platelets. However, delamination is generally detrimental to the fluidity of clay pigments in high solids clay-water slurries. Good fluidity at high solids concentration is very desirable and often necessary for clay pigments in their paper coating applications^[8]. Therefore, with the use of conventional delaminated pigments, papermakers must balance the trade-off between paper quality and efficiency of production.

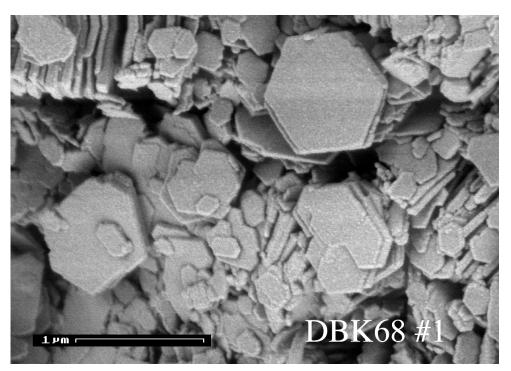


Figure 2. SEM of clay^[11]

3.2 Coating binders

Binders are the second most abundant component in coating colour after the pigment. The most important aims for its application in coating colours are the binding of pigment particles to base paper, the binding of pigment particles to each other, partial filling of voids between pigment particles (porous coating structure) and affecting the viscosity and water retention of the coating colour.^[5.] Binder provides the strength required for coated paper to pass through printing and

converting operations. It also influences coater runnability and coating rheology. As pigments, one or more binders can be used in coating colour. Some common binders used for coating paper are classified by their origin and solubility in water:

- Not soluble in water (Styrene butadiene latex, Styrene acrylate latex, Polyvinyl acetate latex)
- Soluble in water (Starch, Carboxy methyl cellulose, Polyvinyl alcohol)

Latex is a water-based polymer of very small spherical polymer particles (30-500 nm) with different chemical compositions of the sphere nucleus. It is also called emulsion polymer and dispersions. Latex is an amorphous and viscoelastic material with a glass transition temperature (T_g) between -7 and 40°C, depending on component polymers. Polymer based on styrene-butadiene (SB latex) is very common, especially for products destined to lithography printing due to the superficial strength and printability required, but it can be also used for rotogravure and flexography. SB latex-based coating systems offer high coating speed and enhanced pigment binding power that results in smoothness, higher gloss level, brightness, opacity and water resistance at a lower cost than alternatives. The compositions can be of styrene-butadiene copolymer, cross-linked styrene-butadiene, and others. The components ratio in the copolymer is generally 70% of styrene and 30% of butadiene. The surface chemical composition of the binder spheres is also differentiated by the adsorption of anionic surfactants, which are used as stabilizing aids of the dispersion in water. [12.]

For paper coating applications, in order to correlate the properties of both wet paper coating formulations and coated paper, additional SB latex properties are often needed to be characterized such as surface tension colloidal properties, mechanical properties of latex films, thermal and viscoelastic properties, etc. During the drying of the coating, latex is melt producing a film that embraces pigment particles on the surface and thus forming the paper coating. Adhesion between latex and inorganic pigments (clay) are influenced by the coating drying temperature, latex glass transition temperature, and surface properties of latex and pigment. Pigment particles are coated by a latex film when the temperature in drying conditions is higher than the latex T_g . Interactions between the film and

the particle are dependent on the pigment superficial groups and the amount of acidic groups on the surface of the latex micro-sphere. A poor adhesion is observed in conditions of drying with temperature lower than the latex T_g , causing a partial surface coverage of the pigment^[14].

3.3 Coating dispersants

The role of the dispersing agent (dispersant) is an additive to make the dispersion process easier and more stable. Dispersants de-flocculate solids and thus significantly reduce the viscosity of a dispersion. As a result of this effect, solid loading – the amount of dispersible powdered material – can be increased accordingly. The dispersion phase is possibly the most time- and energy-consuming stage of the production process. This is due to the different surface tensions of the liquids and the solids. A dispersing additive is necessary to produce stable formulations and ensure storage stability (no viscosity instability, no separation)^[15].

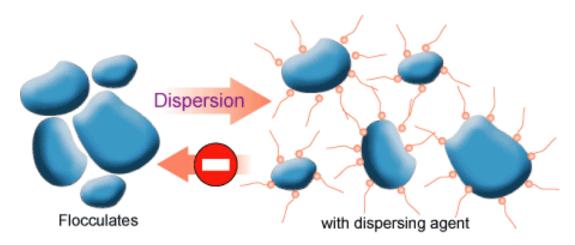


Figure 3. Dispersing agents avoid flocculation^[16]

Stabilization is achieved through absorption of stabilizing molecules on the pigment surface, so that repulsive forces prevent other particles from approaching close enough for the attractive van der Waals forces to cause agglomeration. Possessing kinetic (thermal) energy and being subjected to Brownian movement, colloid

particles persistently approach one another and collide. Without restricting factors, their approachability may occur so close that even relatively short-range van der Waals forces will be capable to join particles irreversibly, thereby destroying the dispersion. Alternatively, having a certain source for inter-particle repulsion, capable to prevent particles from immediate contacts, dispersion can persist indefinitely without significant changes in particle size and properties. The existence of sufficient repulsive forces between neighbouring colloid-size particles is therefore a matter of life or death for any dispersion. Those repulsive forces arise when lyophilized near-particle layers interfere the persistent exchange of the molecules of water between the near-surface layer and the non-changed water outside the layer creates the repulsive force, similar to osmotic pressure. [16.]

Sodium polyacrylate is salt of polyacrylate acid. It is used as dispersant because the solids loading can be increased to 75 wt. % while maintaining the desired viscosity.

3.4 Rheology of pigment slurries and rheological properties of coating colours

Coating colours are traditionally studied using rheology techniques^[13]. Rheology is defined as the science of the deformation and flow of matter, that is, how materials respond to the stresses applied to them^[5].

Rheology plays different roles at different stages in the life of coating pigments and coating colours as they move from storage to coating^[17]. Viscosity is the key rheology property for paper coatings. It is important to recognize that viscosity is a curve, not just a number. The curve represents the change in viscosity as a function of shear rate or shear stress^[5]. A long range of shear rate must be tested for a complete evaluation and this constitutes an experimental difficulty, once that the current measurement devices are suitable only for the extremes of low and high shear rates. Coating components are particles not symmetrical that present size, form and cohesiveness as factors that affect the force necessary to put them into motion in a flow.

Paper coating is a thixotropic fluid and it must behave in a way that coating colour flows only at the moment and at short instants after its application in conditions of high shear rates. The flocculated structure of the fluid is destroyed as function of time during the shearing in a way that the viscosity is lower than the observed one during the increase in shear rate. Flocks can reorganize again after the structure breakage and the time needed to this restructure affects the return of viscosity to the previous values. If the flock restructure is achieved fast then viscosity keeps a constant platform, but if the linkages are restored slowly then the viscosity is reduced.[13.]. The reestablishment of the linkages depends on the interface between the dispersed phase and the liquid phase and also the pigment particles size and its distribution, particle shape and its distribution, pore size and its distribution, polymers and other molecules adsorbed on pigment surface, and polymer dissolved in the liquid^[17]. Although coating colours with lower viscosities in the high shear rate range usually have better runnability, running coating colours at the highest solids level possible is more economical. The choice of coating colour solids is often a compromise, although rheology modifiers, lubricants, and other additives can fine-tune rheology while preserving coated sheet properties^[17].

4 EXPERIMENTAL PART

The experimental part describes the raw materials and machinery using during the test and the procedures of the whole work.

4.1 Materials

Clay (SPS, English China Clays, ρ = 2.59 g/cm³) was used as pigment.

Sodium polyacrylate (Lopon 890, BK Giulini, ρ = 1.3 g/cm³) was used as dispersing agent.

Styrene-butadiene latex (DL-950, DOW Chemicals, ρ = 1.0 g/cm³) was used as binder. In the dispersion, the solids content was 50% by weight.

The distilled water of NaOH content of 2 g/dm³, pH = 13.3

Two base papers were used: white printing paper (basic weight $\approx 80 \text{ g/m}^2$, Cobb₆₀ $\approx 40 \text{ g/m}^2$), and brown gummed paper (basic weight $\approx 50 \text{ g/m}^2$, Cobb₆₀ $\approx 30 \text{ g/m}^2$).

4.2 Procedures

The procedures consists four steps, including coating preparation, thickness and basis weight measurements, optical measurement, and water penetration measurement.

4.2.1 Coating preparation

At the beginning of the experimental work of this study, coated paper samples were prepared in laboratory scale.

Mixtures of pigment (clay), dispersant agent (Lopon), binder (Latex), and distilled water with NaOH formed coating colours. Those mixtures were prepared in the following formulations:

- Level of dispersing agent: 1 pph

- Latex content: 2, 10, 20, 50, 100 pph

- Solids content: 30% by volume

The dispersion of pigment was prepared at high solids content of 75-80% by weight.

Concentration of electrolytes and pH of the medium affect the dispersion properties. After coating colours were formed, the used distilled water of NaOH and coating colours were measured pH with pH-meter, model pH Scan1, Eutech Instruments Pte. Ltd.^[ii]

A coating layer was applied on the base paper using a transfer rod lab coater^[18] (K rod No. 3) with single sided coating (one layer). After coating colour transfer, the water was removed by treatment with heat (IR radiation). During the coating colour transfer, excellent flow properties of fluidity were required, which was reached due to low solids and viscosity. Finally, five good samples of a size of A5 of each kind of paper were chosen for each formation for further experiments. After drying, all paper samples were placed in a room with constant temperature (23 \pm 1°C) and constant relative humidity (50 \pm 2%)^[i].

4.2.2 Thickness and basis weight measurements

Thickness and basis weight measurements were second steps to observe the physical change of coated papers compared to base papers.

After staying in constant temperature and humidity room, all paper samples were cut into 10x10 mm squares for thickness and basis weight measurements. Ten samples were prepared for every formulation.

Thickness test^[iii] was done in constant temperature and humidity room. Base papers and all types of coated papers were tested. Five measurements for each type of paper were performed in different positions using Lorentzen & Wettre (Sweden) apparatus and the average values were calculated.

For basis weight test^[iv, v], base papers and each formulation of coated paper were weighed with laboratory balance.



Figure 4. Thickness tester (Lorentzen & Wettre, Sweden)

4.2.3 Optical measurement

Optical measurement investigates the impact of coating on papers' performance (brightness, reflection, and opacity).

After thickness and basic weight measurements, the optics of all paper samples was examined. For each formulation, 10 tests were recorded in different positions to obtain the average values.

White printing papers were tested by spectrophotometer SpectroEye, GretagMacbeth. The reflection coefficients (remission curves) were recorded with

observer 10°, illuminant D65 and filter D65. The ISO brightness was recorded with observer 2°, illuminant C and filter D65.

Reflection coefficient R_0 of brown gummed papers was recorded by Leucometer Elrepho, Opton 65746 with blue filter^[vi].

4.2.4 Water penetration measurement

This experiment was used for investigating the dynamics of the penetration of uncoated and coated papers.



Figure 5. Sample holder

Five samples of white printing papers were prepared for every formulation with the size of 50x75 mm. All measurements were done with PDA Module S05, Emtec GmbH^[19, 20] (fig. 6). The apparatus was switched on 10 minutes before the measurement. Measuring cell was filled up with water as test fluid, to upper mark

(filling level 1 for long immersion way). The doubled-sided adhesive tape was stuck on the sample holder according to the marks (fig. 5). Then, a sample was laid on sample holder with the coated side on the top. Air bubbles between sample and holder were removed with pad roller. The clamp of the apparatus was lifted in the start position. Sample holder was inserted vertically into the clamp of the immersion device. The immersion was started by pressing of the right part of the lever. The measurement happened in 60 seconds. All results were recorded by programme in computer. After the measurement, the clamp was pulled with the handle into the upper starting position and sample holder was removed. Each type of coating paper was measured at least 3 times to obtain similar curves.

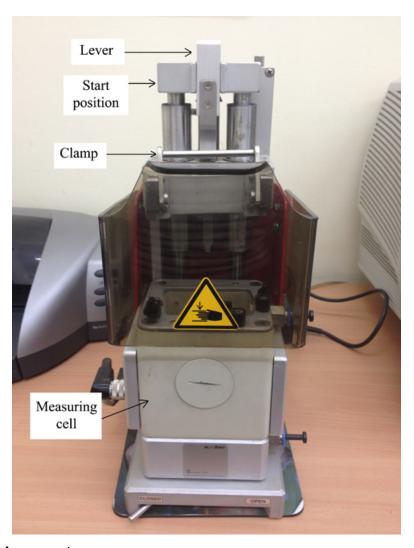


Figure 6. PDA apparatus

5 RESULTS AND DISCUSSIONS

In this part, all the results were presented and discussed to see how the ratio of clay/latex affects on properties and absorption characteristics of coated papers.

5.1 Thickness and basis weight measurements

Thickness and basic weight measurements are the basic physical changes when applying coating colour on paper surface.

5.1.1 Thickness measurement

Applying coating colour on paper surface means a thin layer presented on paper surface. This layer eventually changes the original thickness of paper.

According to figure 7, coating thicknesses of all types of papers are plotted. The figure shows the decline of coating thickness with the rise of latex content in coating. With low density (1.0 g/m²), the population of latex particles is less than clay particles population in the same area. Moreover, latex particle shape is smaller than clay particle shape. There is more space between those particles, which makes the coating layer thinner. Therefore, this reduces coating thickness when latex content increases and the amount of clay decreases. Coating with 2 pph of latex content has thickest coating layer on paper with 6.9 μ m. Coating thickness of coating of 10 pph, 20 pph and 50 pph are 5.9 μ m, 4.3 μ m and 3.7 μ m, respectively. Coating with 100 pph has thinnest coating layer on paper with 3.3 μ m.

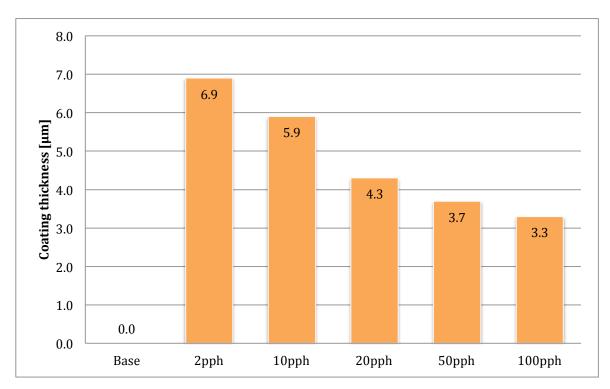


Figure 7. Coating thickness of PWPW papers

There is the same trend for brown gummed papers' coating thicknesses presented in figure 8. Coating layer will make paper thicker than the original one. However, the coating thickness also depends on the ratio of clay and latex. The bigger the latex content in coating is, the thinner the coated paper is. For examined gummed papers, the thickest layer (8.7 μ m) is paper with 2 pph of latex content in coating. Coating thickness of coating of 10 pph, 20 pph and 50 pph are 7.5 μ m, 5.9 μ m and 4.3 μ m, respectively. And the thinnest layer (3.3 μ m) is paper with 100 pph of latex content in coating.

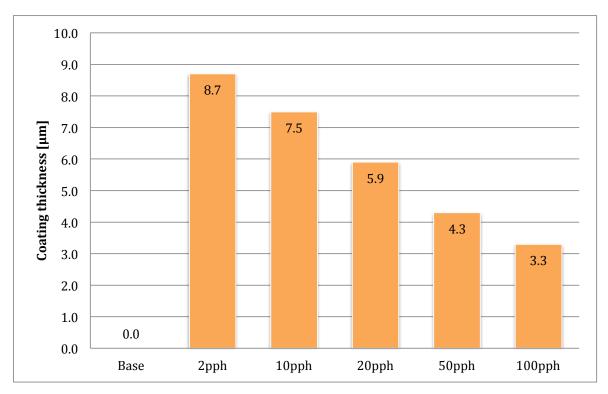


Figure 8. Coating thickness of gummed papers

On the other hand, with the same latex content, brown gummed papers seem thicker than white printing papers. The discrepancy between two kinds of coating papers with the same latex content is in the range of 0.6 μ m and 1.8 μ m. However, there is the same thickness (3.3 μ m) for both white and brown coating of 100 pph of latex content.

5.1.2 Basis weight

Coating layer also changes the basic weight of paper physically. The coating weights of white printing and brown gummed papers were plotted in figure 9 and 10, respectively.

As presented in figure 9, coating weights reduce gradually with the decrease of clay content in coating colours. Coating colour with lowest latex content (2 pph) gives coated weight of 19.8 g/m² as the heaviest. On the other hand, coating colour with highest latex content (100 pph) gives coated weight 12 g/m² of coating on paper as the lightest one. According to this observation, the densities of clay

and latex are considered again as the main factor for this change. In the dispersion of clay and latex, clay with high density (2.59 g/cm³) affects the weight of the dry coating much more than latex with low density (1.0 g/cm³) does. With the decline of clay and the rise of latex content, fewer clay particles take part in the dispersion and the coating weights are decreased as a result of this fact.

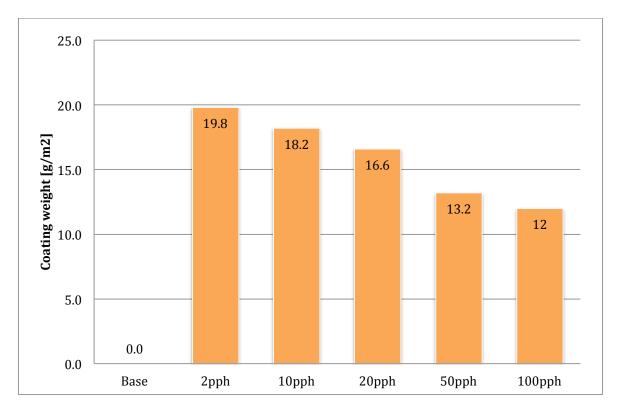


Figure 9. Coating weight of white printing papers

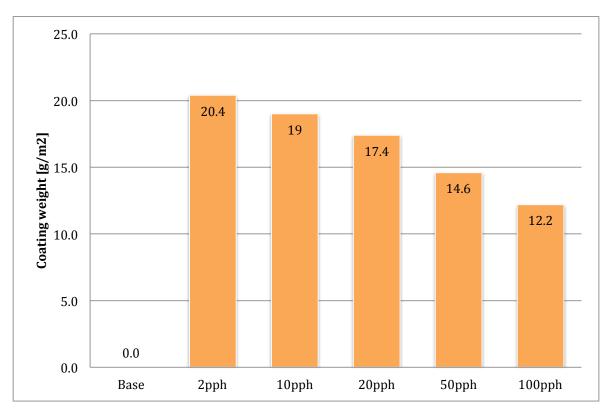


Figure 10. Coating weight of brown gummed papers

Figure 10 shows the similar tendency for brown gummed papers. The coating weight depends on the ratio of clay and latex. The coating weights decrease with the increase of latex content. Coating weights decline gradually from 20.4 g/m^2 to 12.2 g/m^2 for coating of latex content from 2 pph to 100 pph. Coating weights coatings of 10 pph, 2 pph and 50 pph of latex content are 19 g/m², 17.4 g/m^2 and 14.6 g/m^2 , respectively.

Then again, even though basis weights of brown base papers are lighter than the white one, the coatings give conflicting results. Basis weights of brown coatings are heavier than those of white ones. The discrepancy between two kinds of coatings papers having the same latex content is approximately 0.2 μ m to 0.8 μ m.

5.2 Optical measurements

Optical measurements, including reflection coefficient, ISO brightness and opacity tests, present the final look of coated paper. These properties are quite important for printing papers since they show how printing inks appear and affect to human eyes.

5.2.1 Reflection coefficient

When light strikes a paper structure, some light is spectrally reflected and the remainder enters the fibre bonds. The light scatters in all directions. Some light returns from the structure and the remainder is transmitted or absorbed. Therefore, reflectance measurements are used to determine the reflected, either transmitted or absorbed intensity of lights^[21].

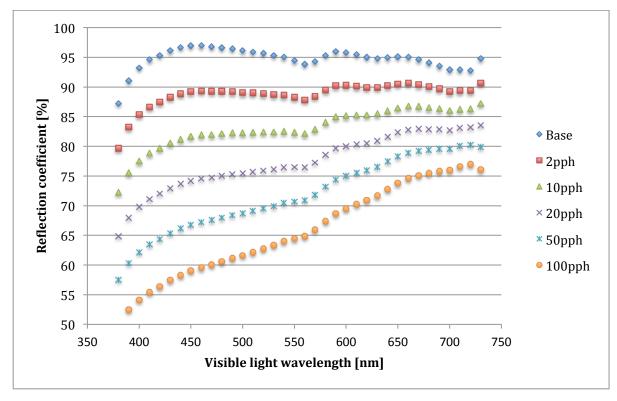


Figure 11. Plot of reflection coefficient of white printing papers as function of visible light wavelength (remission curves)

The remission curves of white printing papers are shown in figure 11. In general, uncoated and coated papers have similar shape of curves. However, clay and latex have similar refractive index (1.55), which lights cannot reflect much. Consequently, reflection coefficients of coated papers are lower than uncoated papers. On the other hand, coating colours, which have high latex content, give low reflection coefficient of coated papers. Latex film is translucent, which prevents lights reflect. Therefore, the bigger the latex content in coating is, the lower the reflection coefficient of paper is. Generally, the reflection coefficients of examined papers are quite low in the blue light region (450 - 495 nm) and higher at the red light region (620 - 730 nm). The reflection coefficients reduce appropriately from 80 - 90% to 50 - 75% with the growth of latex content. Moreover, the bigger the latex content is, the bigger the discrepancy of reflection coefficient in visible light range is. Reflection coefficient values of coating with 2 pph of latex content are quite similar in the whole range of visible lights (380 - 730 nm), which is from 79.7% to 90.6%. The discrepancy of reflection coefficient values of coating with 10 pph, 20 pph, and 50 pph of latex content in the whole range of visible lights are 15%, 18.7%, and 22.4%, respectively. The biggest change is coating with 100pph of latex content, from 49.8% at 380 nm to 76% at 730 nm.

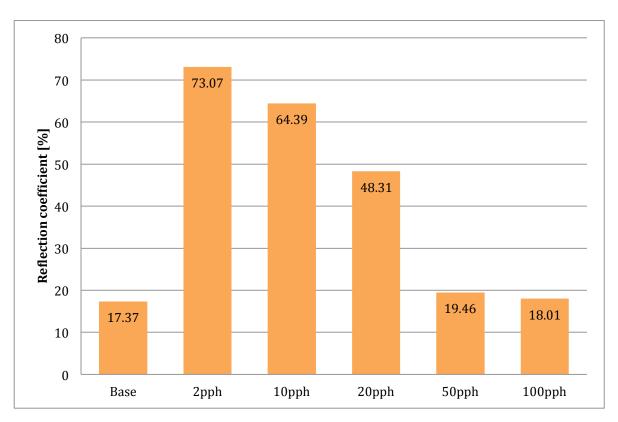


Figure 12. Reflection coefficient of brown gummed papers

Similar observation reflection coefficient of coated gummed papers is in figure 12. The more the latex content is, the lower the reflection coefficient of paper is. With coating of very high latex content (50 pph and 100 pph), the reflection coefficient values drop more than half of the previous one (20 pph). Unmistakably, coating with 2 pph of latex content gives the highest reflection coefficient value (73.07%), whilst coating with 100 pph of latex content gives the lowest reflection coefficient value (18.01%). From another point of view, for uncoated gummed paper, its reflection coefficient is very low compared to the coated one. Tested gummed papers are brown, which is not bright and cannot reflect much light. Therefore, when applying coating colour with white pigment such as clay, the colour of gummed paper is changed and it makes papers look brighter. The coating layer also helps to increase the reflection coefficient of brown paper maximum of 55.7%.

5.2.2 ISO brightness

Brightness is one of the most important optical properties of paper. Brightness of coated and uncoated white printing papers used in this study is measured as ISO brightness, which is measured as a percentage of absolute whiteness. ISO brightness is the amount of light reflected from the fibre bonds of a paper as compared to the amount of blue light (457 nm) that strikes in the paper structure.

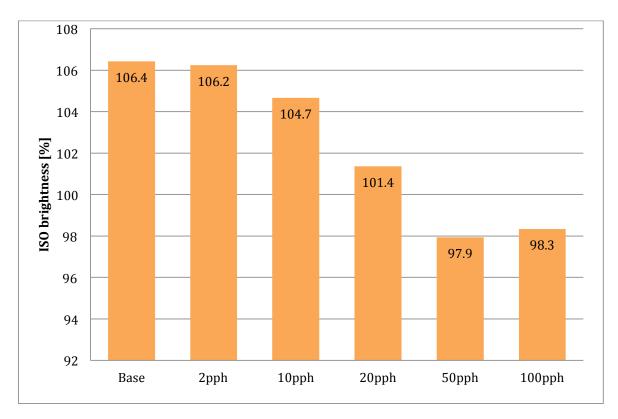


Figure 13. ISO brightness of white printing papers

Figure 13 shows the ISO brightness of PWPW papers. It is obvious that coating layer prevents the lights from reflecting from fibre bonds. Therefore, ISO brightness of coated papers is lower than uncoated papers. Moreover, because latex is opaque agent, the bigger latex content in coating is, the smaller ISO brightness paper has. These results are related to the reflection coefficients of white printing papers in the previous part since its reflection coefficients are quite low in blue light region (457 nm). For coated papers, coating with 2 pph of latex content shows the highest ISO brightness value (106.2%). Compared to uncoated paper, ISO

brightness of coating with low latex content (2 pph) just slightly decreased by 0.2%. The bigger latex content is, the bigger discrepancy there is between two sequent coatings. ISO brightness of coating with 10 pph and 20 pph are 104.7% and 101.4%, respectively. Coating with 50 pph of latex content showed the lowest ISO brightness value (97.9%). However, ISO brightness of coating with 100 pph of latex content (highest amount of latex content in coating colour) seemed to increase lightly again to 98.3%. This value makes a small change for whole observation and need to be studied more for a real consequence.

5.2.3 Opacity

As brightness, opacity is one of the most important optical properties of paper. Opacity measures the ability of the paper to conceal text on the other side of the sheet^[21]. In other words, paper which lets a lot of light through, is transparent; paper that lets little light through, is opaque. The higher the value is, the more opaque the paper is.

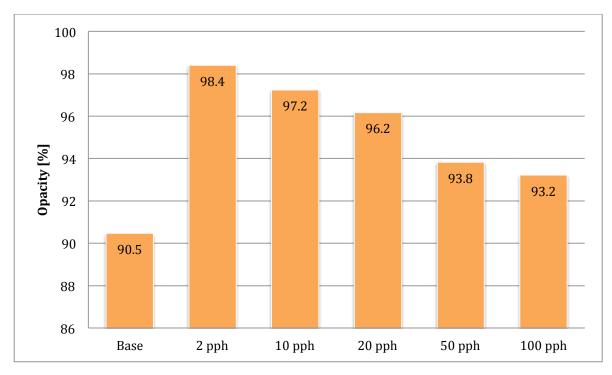


Figure 14. Opacity of white printing papers

The opacities of uncoated and coated white printing papers were performed on figure 14. Generally, opacity and brightness are inversely related to each other. From the results of the previous part (ISO brightness), we can see the relationship between brightness and opacity. Coating layers reduce coated papers' brightness but help to increase its opacity. Compared to base papers, opacity of coated papers was much higher than uncoated one. Coating layers increased opacity of coated papers by approximately 8%. However, with the growth of latex content in coating, opacity of coated papers declined gradually. Latex film is translucent. Hence, the bigger the latex content is, the more translucent the coating layer is. This latex film will reduce the opacity of coated paper. Opacity of coating of 2 pph of latex content was 98.4% as the highest value. Opacities of coating of 10 pph, 20 pph and 50 pph were 97.2%, 96.2% and 93.8%, correspondingly. The one of 100 pph of latex content was 93.2% as the lowest value.

5.3 Water penetration

Absorption of aqueous solutions into paper coatings is important in a number of printing technologies, not only inkjet printing but also flexography where aqueous based inks are frequent, and offset printing where the aqueous fountain solution has a strong impact on printability^[22].

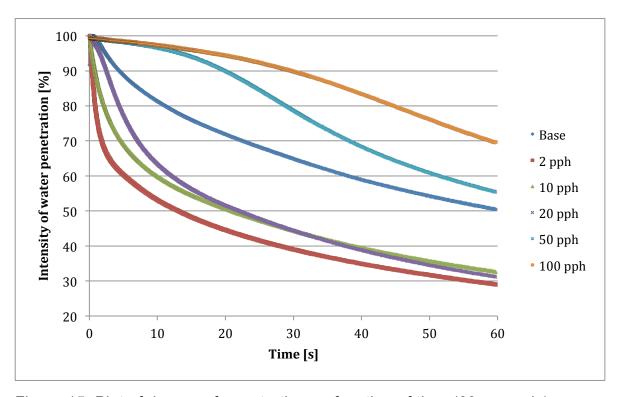


Figure 15. Plot of degree of penetration as function of time (60 seconds)

In general, the penetration of water into paper within 60 seconds was presented in figure 15. Uncoated paper has general penetration with the wetting delay time because of air trapped onto the paper roughness. The wetting of uncoated paper is 1 degree. Nonetheless, coated papers are 0 because they do not have the wetting delay time. Coatings of low latex contents (2 pph, 10 pph, and 20 pph) absorb more water than uncoated one, while coatings of high latex contents (50 pph and 100 pph) absorb less water than uncoated one. Moreover, the times till maximum absorption are recorded in figure 16. Because of wetting delay time, uncoated paper needs more time to let water go through the fibre pores than coated one. Maximum time for uncoated paper is 0.61 second. For coated papers, the times till maximum penetration increase gradually with the increase of latex content in coating. Coatings of 2 pph and 10 pph time maximum are 0.07 second as the fastest absorption. Coatings of 20 pph and 50 pph time maximum are 0.12 second and 0.16 second, respectively. Coatings of 100 pph time maximum is 0.28 second as the lowest absorption compared to other coatings.

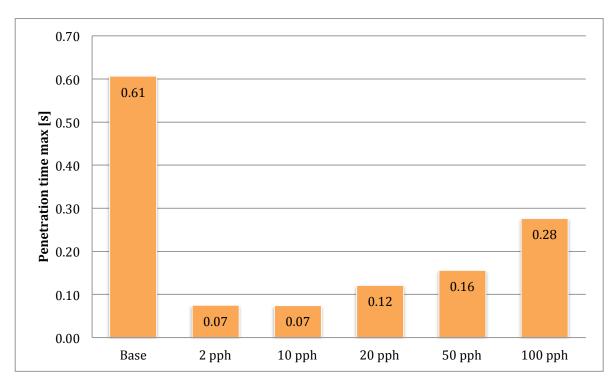


Figure 16. Time till maximum penetration

In order to examine the ability of absorption for printing since water / ink absorbs very fast at the beginning of the process within 1 to 2 seconds, the penetration of the first and the last 2 seconds were considered as the biggest changes. The degrees of penetration for first and last 2 seconds were plotted in figures 17 and 18, respectively.

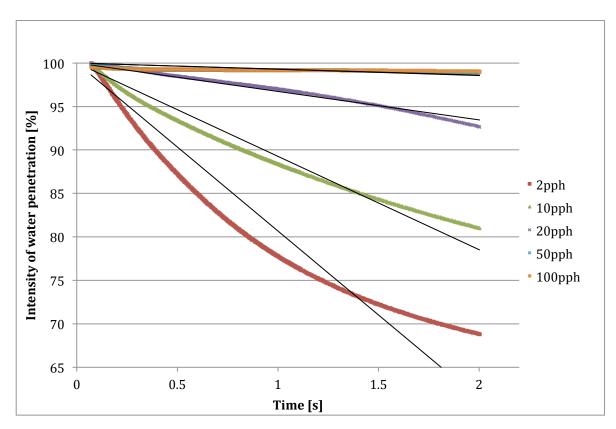


Figure 17. Plot of degree of penetration as function of time for first 2 seconds

Table 2. Curves' equations and R-squared values

Latex content	Equation	R ²
2 pph	y = -19.324x + 100	0.87735
10 pph	y = -10.737x + 100	0.95557
20 pph	y = -3.2717x + 100	0.98287
50 pph	y = -0.7223x + 100	-2.3676
100 pph	y = -0.6976x + 100	-11.503

For the first 2 seconds, as we can see in figure 17, the degree of penetration of coating of 2 pph and 10 pph are extremely fast with the high slopes of 19.324 and 10.737, correspondingly. Coating of 20 pph absorbs less water than two previous ones with the slope of 3.2717. Moreover, the degree of penetration curve of this coated paper gets the good fit for the trend line with 0.98 for R² value compared to other kinds of coated papers. Clay particles are very small with pseudo-hexagonal shapes, which are a tremendous surface area. Large amounts of clay together create lots of tiny in-between spaces. The increased amount of spaces between

clay particles creates abundant surface area on which water molecules can adhere^[23, 24]. Thus, coatings of 2 pph, 10 pph and 20 pph of latex content with higher amount of clay particles than the remaining can absorb much more water than other types of papers. On the other hand, coatings of high latex content (50 pph and 100 pph) absorb excessively less water with very low slopes (0.7223 and 0.6976, respectively). As mentioned in theory part, latex is a water resistant agent. Hence, the bigger the latex content in coating is, the less water absorption there is through paper. In other words, high latex and low clay contents in coating reduce the ability of absorption liquid through the fibres structure.

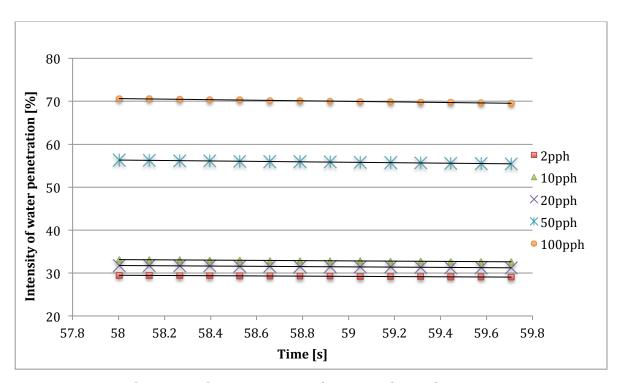


Figure 18. Plot of degree of penetration as function of time for last 2 seconds

Table 3. Curves' equations and R-squared values

Latex content	Equation	R^2
2 pph	y = -0.2493x + 43.937	1
10 pph	y = -0.2967x + 50.335	1
20 pph	y = -0.3105x + 49.759	1
50 pph	y = -0.5107x + 85.935	0.99999
100 pph	y = -0.64x + 107.76	0.99999

For the last 2 seconds of penetration shown in figure 18, as time passes, the degrees of penetration of all types papers increase. At the end of the penetration time, the degrees of penetration are nearly linear since those examined papers reach their limit for absorption liquid. Coatings of 2 pph, 10 pph and 20 pph absorbed approximately 70-75% of water. At the beginning, coating of 10pph latex content seemed absorb more water than the one of 20 pph, however, coating of 20 pph's degree of penetration increased more than the one of 10 pph at the end of time. This observation needs to be examined in more detail to understand the real phenomenon. The first three levels of coatings' degrees of penetration curves also show perfect fit trend lines with 1 for R² value. Uncoated paper's degree of penetration approaches 50%. Coating of 50 pph of latex content absorbs around 53% more water than at the beginning. Coating of 100 pph of latex content just takes up nearly 28% than at the beginning as the lowest absorption paper. With the increase of latex and reduction of clay, coatings become more resistant to water.

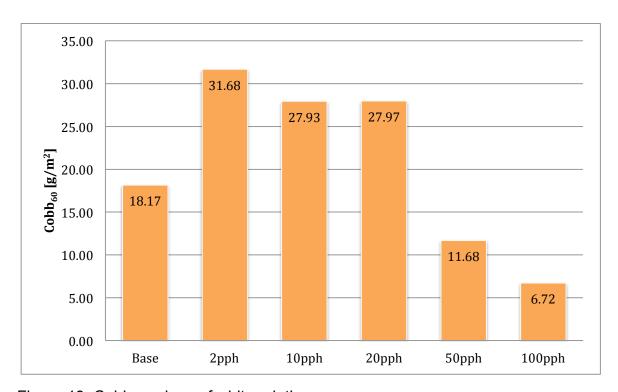


Figure 19. Cobb₆₀ values of white printing papers

According to the degrees of penetration above, the Cobb₆₀ values of all types of papers were measured and plotted in figure 19. Cobb₆₀ value indicates the ability to absorb water on one side of a paper sheet within $60s^{[25]}$. Similarly, Cob_{60} value of uncoated papers is quite low compared to coated papers, which is 18.17 g/m^2 . Cobb₆₀ value of coatings of 2 pph of latex content is the highest with 31.68 g/m^2 . The Cobb₆₀ value of coatings of 10 pph of latex content, however, is a bit lower (27.93 g/m^2) than the one of 20 pph (29.97 g/m^2) . This observation is related to the degree of penetration curve for the last 2 seconds, since coating of 20 pph absorbs more water than the one of 10 pph. Three kinds of coatings contain large amount of clay particles, which can improve the ability to absorb water of papers. Nevertheless, the growth of latex in coatings declines the Cobb₆₀ value rapidly because of water resistance characteristic of latex. Coating of 50 pph of latex content's Cobb₆₀ value is 11.68 g/m^2 , which is equal to more than half of the base value. Coating of 100 pph of latex content's Cobb₆₀ value is 6.73 g/m^2 , which is just half of the previous one (50 pph).

6 CONCLUSIONS

At the beginning of this study, 5 kinds of coating papers were prepared with different ratios of clay and latex in coating colours. The latex content was from 2 pph to 100 pph. Later, to examine the effect of clay and latex ratio on hiding power and absorption characteristics of coated papers, the measurements of thickness, basis weight, optics, and water penetration were carried out.

For thickness and basis weight, coating layers increase the thickness and basis weight of coated papers, generally. Moreover, because latex density (1.0 g/cm³) is much lower than that of clay (2.59 g/cm³), the population of latex particles are sparser than clay particles. Therefore, with the growth of latex content in coatings reduced the thickness and basis weight of coated papers gradually.

For the optical properties, the reflection coefficient / remission curves, ISO brightness, and opacity were tested. All measurements were recorded for visible wavelength (380 - 730 nm) range. Because latex film is translucent, it lets more light go through the paper structure. Consequently, the bigger the latex content in coating is, the lower the reflection coefficient, ISO brightness, and opacity of coating papers are. To be more specific, the remission curves of white printing papers are lower than those for uncoated papers because clay and latex with similar refractive index (1.55) cannot reflect much light. Besides, the reflection coefficient values are quite low at the blue region (450 – 495 nm) and higher at red region (620 - 730 nm). Nonetheless, with brown gummed papers, coatings help to increase their reflection coefficient because their surface was covered by white pigment (clay). On the other hand, ISO brightness was tested for only white printing papers. ISO brightness was measured for blue light (457 nm) of visible wavelength. Coated papers' ISO brightness is lower than that of uncoated ones. These results are related to the low value of reflection coefficient in blue region of white printing papers. Moreover, a small experiment should be done to explain the slight increase in brightness of coating of 100 pph of latex content. In addition, brightness and opacity are inversely related to each other. Coating of 2 pph of latex content helps to increase the opacity of paper approximately by 8%. Later, the opacity reduces gradually with the increase of latex content.

Finally, water penetration of white printing papers was measured. Uncoated papers get wetting delay time because of air trapped onto paper roughness. Coating of 2 pph and 10 pph of latex content absorbed water extremely fast. Coating of 20 pph absorbed less water than the one of 10 pph during the first 2 seconds, however, the amount of absorbed water increased at the last 2 seconds. Water penetrated excessively slowly through coating of 50 pph and 100 pph. Since latex is a water resistant agent, high latex content in coatings will prevent the absorption of water. Additionally, the Cobb₆₀ values were recorded to examine the ability to absorb water of coatings. Generally, Cobb₆₀ values of 2 pph, 10 pph, and 20 pph coated papers were higher than those of uncoated ones. On the other hand, the ones of coating 50 pph and 100 pph were lower than uncoated. Related to the penetration curves, the bigger the latex content is, the lower the Cobb₆₀ value is. However, Cobb₆₀ value of coating of 20 pph is higher than the one of 10 pph, since it absorbs more water at the end of penetration time (last 2 seconds). Again, this observation should be studied more for the final conclusion.

Briefly, this study has pointed out some key aspects of coated papers' behaviour when applying different ratios of clay and latex in coating colour. Depending on the application of paper product, especially in printing industry, the ratio of clay and latex in coating colour is crucial for the improvement of the coated paper's characteristics (thickness, basis weight, optics, and water penetration).

7 REFERENCES

- Introduction of The Institute of Papermaking and Printing at the Technical University of Łódź, Poland. Retrieved from www.inpap.p.lodz.pl on 17th March, 2013
- Wilson I., Filler and Coating Pigments for Papermakers. Retrieved from http://wakaolin.com/Website%20pdfs/IRW%20PAPER%20PIGMENTS%20 %20SME%202006.pdf on May 8th, 2013
- Ahokas M. 2011. Enhancing Performance of Paper Coatings by Tailor-made Plastic Pigments. Turku, Finland. Retrieved from http://www.doria.fi/bitstream/handle/10024/69760/ahokas_mia.pdf?sequenc e=1 on May 9th, 2013
- Omya Switzerland, Coating pigments. Retrieved from http://www.omya.com/C12574C800504229/vwWebPagesByID/24A33068C0 74B5F9C1257363005A8134 on May 8th, 2013
- 5. Gullichsen J., Paulapuri H., Lehtinen E. (editors), 2000. "Papermaking Science and Technology: Book 11: Pigment Coating and Surface Sizing of Paper", joint work, Fapet Oy, Helsinki, Finland
- 6. Hagemeyer, R., Ed. 1997. Pigments for paper; TAPPI press: Atlanta, 1997
- 7. Al-Ani, T.; Sarapää, O. 2008. Clay and Clay Mineralogy. Physical-chemical Properties and Industrial Uses.; GTK: Espoo, Finland
- Jun Yuan et al. 2002. Kaolin Clay Pigment for Paper Coating and Method for Producing Same (June 11th). Retrieved from http://www.google.com/patents/US6402826 on May 9th, 2013
- 9. Aline, B. and Lepoutre, P. 1980. Porosity and Optical Properties of Clay Coatings, J. Coll. Interf. Sci., 76(2), p. 439
- 10. Lehtinen, E., Ed. 2000. Pigment Coating and Surface Sizing of Paper, Fapet ov: Helsinki
- 11.SEM of clay. Retrieved from http://www.gly.uga.edu/Schroeder/geol6550/DBK.html on May 9th, 2013

- 12. Joanicot, M., Wong, K. and Cabane, B. 1993. Structure of latex films, Proc. TAPPI Coating Cond., p.383
- 13. Fardim P., Paper and Surface Chemistry Part 2 Coating and Printability.

 Retrieved from
 http://www.tappi.org/content%5CJournal%5C2002%5CTJ%5C09sep02%5CFardim2_Eng.pdf on May 11th, 2013
- 14. Granier, V. V., Sartre, A., Joanicot, M. M. 1994. Adhesion of latex particles on inorganic surface, TAPPI J., 77 (5), p. 419
- 15. Dispersing agents, BASF The Chemical Company. Retrieved from http://www.dispersions-pigments.basf.com/portal/basf/ien/dt.jsp?setCursor=1_556356 on May 14th, 2013
- 16. Dispersing process. Retrieved from http://www.inkline.gr/inkjet/newtech/tech/dispersion/#colloidal on May 14th. 2013
- 17. Tamal, G. 1998. Pigment Slurries and the Coating Colours they Form: Part 2, TAPPI J., 81(8), p.123-126
- 18. RK Print Coat Instruments Ltd. Materials
- 19. Grüner G. 1996. "Emtec Penetration-Dynamics Analyzer", Emtec Electronic GmbH materials, Leipzig, Germany
- 20. PDA manual
- 21. Optical properties. Retrieved from https://docs.google.com/viewer?a=v&q=cache:5eankv4kLl8J:www.wmich.ed u/ppse/staff/courses/fleming/Lec4.ppt+&hl=en&pid=bl&srcid=ADGEEShuP4 szPWnt93QxS605u1GRzkESPEGnotcuplGXbwNa5R6WU4nQCMggaSM0X lbZ7U74ZFbWcsFSSyiHtOC8tfg-kN3GAZ5Q8Xza37BjNAsmpaiK4rMVpUlng8PCgrjG_dCX1DCF&sig=AHIEtb T90Xl3updLuXs5pC53B6aAKHpueg on May 18th, 2013
- 22. Ström, G. R., Borg, J. and Svanholm, E. 2008. Short-time water absorption by model coatings, Sweden. Retrieved from

- http://www.tappi.org/Downloads/Conference-Papers/2008/08ADV/08adv18.aspx on June, 24th, 2013
- 23. Stakland, S., eHow. Retrieved from http://www.ehow.com/info_8659157_clay-absorb-water-top-soil.html on June 25th, 2013
- 24. Barshad, I., Bull. Vol. 169. Adsorptive and swelling properties of clay-water system, p. 70-77. Retrieved from http://www.clays.org/journal/archive/volume%201/1-1-70.pdf on June 25th, 2013
- 25. Hahnemühle, Fineart, Germany. A-Z of paper, Interesting facts on paper.

 Retrieved from http://www.tastarsupply.com/files_informational/hahnemuhle_paper_glossary.pdf on June 25th, 2013

8 STANDARDS

- PN-EN 20187:2000 Paper, paperboard, and fibrous mass. Climatic conditions and standardized tests, and how to check the conditions and conditioning of samples. (Papier, tektura i masy włókniste. Znormalizowane warunki klimatyzowania i badania oraz sposób sprawdzania warunków i klimatyzowania próbek)
- ii. ISO 787-9:1981 General methods of test for pigments and extenders –Part 9: Determination of pH value of an aqueous suspension
- iii. **PN-EN ISO 534:2005 (U)** Paper and Paperboard. Determination of the thickness, density and specific volume. (Papier i tektura. Oznaczanie grubości, gęstości i objętości właściwej)
- iv. PN-ISO 536:1996 Paper and Paperboard. Determination of grammage.(Papier i tektura. Oznaczanie gramatury)

- v. **PN-ISO 536:1996/ApI: 1999** Paper and Paperboard. Determination of grammage. (Papier i tektura. Oznaczanie gramatury)
- vi. **ISO 2470:1990** Paper, board and pulps Measurement of diffuse blue reflection factor (ISO brightness)

Appendix 1Data necessary for preparing coating colours

			N° OF C	OATING CO	DLOURS	
		Coated 1	Coated 2	Coated 3	Coated 4	Coated 5
Latex cont.	pph	2	10	20	50	100
Pigment	[g] b.d.	110.81	92.57	76.78	50.78	32.47
	[cm ³] b.d	42.78	35.74	29.64	19.61	12.53
Lopon	[g]	1.11	0.923	0.77	0.51	0.32
	[cm ³]	0.85	0.71	0.59	0.39	0.25
Latex	[g] b.d.	2.22	9.26	15.36	25.39	32.47
	[cm ³] b.d	2.22	9.26	15.36	25.39	32.47
Latex Disp.	[g]	4.43	18.51	30.71	50.78	64.93
	[cm ³]	4.43	18.51	30.71	50.78	64.93
Add. Water	[g]	101.93	95.03	89.05	79.22	72.29
Solids	[g]	113.03	101.83	92.13	76.18	64.93
	[cm ³]	45	45	45	45	45
Total mixed	[g]	116.35	112.01	108.26	102.08	97.72
	[cm ³]	48.07	54.97	60.95	70.78	77.71
Total mass	[g]	218.28	207.04	197.31	181.29	170.01
Solid by weight	[%]	51.78	49.18	46.69	42.02	38.19
Pigment cont. w/w	[%]	50.76	44.71	38.91	28.01	19.10
PVC	[%]	95.08	79.43	65.88	43.57	27.86
рН		8.6	8.1	8.0	7.4	7.0

pH of distilled water with NaOH: 13.3

Appendix 2

Thickness measurement results of white printing and brown gummed papers

	THICKNESS – WHITE PRINTING PAPERS [µm]					
	Base	2 pph	10 pph	20 pph	50 pph	100 pph
	106	115	113	111	115	112
	107	112	113	110	112	111
	108	114	113	111	112	111
	107	113	113	112	109	112
	109	115	112	111	110	111
	110	114	113	113	112	109
	108	115	113	113	109	111
	107	116	114	115	110	110
	107	115	114	110	111	111
	106	115	116	112	112	110
Average	107.5	114.4	113.4	111.8	111.2	110.8
Coating thickness	0.0	6.9	5.9	4.3	3.7	3.3
Standard deviation	1.269	1.174	1.075	1.549	1.814	0.919
Coefficient of variance [%]	1.181	1.026	0.948	1.386	1.631	0.829

	THIC	KNESS -	BROWN	GUMMED	PAPERS	[µm]
	Base	2 pph	10 pph	20 pph	50 pph	100 pph
	87	98	93	92	91	92
	90	97	94	96	92	93
	87	98	96	94	89	92
	88	97	95	96	90	93
	87	98	97	93	88	93
	86	96	98	92	93	91
	89	95	93	90	89	89
	88	96	96	92	95	88
	87	95	96	96	95	89
	88	94	94	95	98	90
Average	87.7	96.4	95.2	93.6	92	91
Coating thickness	0.0	8.7	7.5	5.9	4.3	3.3
Standard deviation	1.160	1.430	1.687	2.119	3.232	1.886
Coefficient of variance [%]	1.322	1.483	1.772	2.264	3.513	2.072

Appendix 3
Basic weight measurement results of white printing and brown gummed papers

	BASIC	WEIGH	T – WHITE	PRINTIN	G PAPERS	6 [g/m²]	
	Base	2 pph	10 pph	20 pph	50 pph	100 pph	
	82	101	100	98	96	93	
	82	102	98	99	95	94	
	83	102	101	98	94	94	
	81	102	100	99	94	95	
	81	101	101	98	96	93	
Average	81.8	101.6	100	98.4	95	93.8	
Coating weight	0.0	19.8	18.2	16.6	13.2	12	
Standard deviation	0.837	0.548	1.225	0.548	1.000	0.837	
Coefficient of variance [%]	1.023	0.539	1.225	0.557	1.053	0.892	

	BASIC WEIGHT – BROWN GUMMED PAPERS [g/m²]						
	Base 2 pph 10 pph 20 pph 50 pph 100 pp						
	63	86	83	80	78	78	
	64	84	82	82	79	75	
	63	84	81	81	77	76	
	65	83	82	82	79	75	
	63	83	85	80	78	75	
Average	63.6	84	82.6	81	78.2	75.8	
Coating weight	0.0	20.4	19	17.4	14.6	12.2	
Standard deviation	0.894	1.225	1.517	1.000	0.837	1.304	
Coefficient of variance [%]	1.406	1.458	1.836	1.235	1.070	1.720	

 $\label{eq:Appendix 4} \textbf{Reflection coefficient R_o measurement results of brown gummed papers}$

	REFLECTION COEFFICIENT R _o – BROWN GUMMED PAPERS [%]							
	Base 2 pph 10 pph 20 pph 50 pph 100 pph							
	17.2	73.1	64.5	48.2	19.5	18		
	17.3	73	65.2	48	19.5	18		
	17.5	73	64.7	48.9	19.4	18		
	17.4	72.6	64.3	48.5	19.3	18		
	17.4	73.1	64.3	48.7	19.2	17.9		
	17.4	73	63.9	48.8	19.3	18.1		
	17.3	72.8	64.5	48	19.4	18		
	17.4	72.6	64.2	48.4	19.5	18		
	17.4	73.8	64.2	47.7	19.7	18		
	17.4	73.7	64.1	47.9	19.8	18.1		
Average	17.37	73.07	64.39	48.31	19.46	18.01		
Standard deviation	0.082	0.403	0.363	0.412	0.184	0.057		
Coefficient of variation [%]	0.474	0.551	0.564	0.853	0.944	0.315		

Appendix 5ISO brightness of white printing papers (pile)

	ISO	BRIGH		ISO BRIGHTNESS - PILE OF WHITE PRINTING					
			PAP	ERS [%]					
	Base	Base 2 pph 10 pph 20 pph 50 pph 1							
	105.8	106.5	104.6	101.1	97.6	98.1			
	106.0	106.3	104.7	101.9	98.3	98.7			
	107.1	106.1	104.9	101.3	97.9	98.8			
	106.8	106.2	104.8	101.2	97.1	97.9			
	106.4	106.2	104.7	101.1	98.2	97.4			
	106.4	106.0	104.5	101.7	98.0	97.3			
	106.1	106.4	104.7	101.2	98.0	99.0			
	106.6	106.6	104.9	100.8	97.5	98.9			
	107.2	105.9	104.3	101.3	98.8	98.6			
	106.0	106.2	104.5	101.9	97.9	98.7			
Average	106.4	106.2	104.7	101.4	97.9	98.3			
Standard deviation	0.5	0.2	0.2	0.4	0.5	0.6			
Coefficient of variance [%]	0.5	0.2	0.2	0.4	0.5	0.6			

ISO brightness of white printing papers (single) using to calculate opacity

	ISO BR	ISO BRIGHTNESS - SINGLE WHITE PRINTING PAPER							
				[%]					
	Base	Base 2 pph 10 pph 20 pph 50 pph 100 pph							
	96.7	104.4	102.0	97.3	91.4	91.0			
	96.5	103.8	102.1	97.2	91.7	92.7			
	96.1	105.7	101.4	97.7	92.9	93.0			
	95.4	104.2	101.7	97.8	91.2	91.1			
	95.7	104.8	102.2	97.2	91.8	92.4			
	97.0	104.6	102.1	97.8	91.4	91.9			
	97.5	104.6	101.6	97.9	92.2	91.0			
	96.3	104.8	101.5	97.3	92.2	91.1			
	95.5	104.5	101.9	97.1	93.2	91.5			
	96.1	104.0	101.4	97.7	90.9	91.1			
Average	96.3	104.5	101.8	97.5	91.9	91.7			
Standard deviation	0.7	0.5	0.3	0.3	0.7	8.0			
Coefficient of variance [%]	0.7	0.5	0.3	0.3	0.8	8.0			

Appendix 6 Opacity of PWPW papers were calculated by $\frac{ISO\ brightness\ of\ single\ papers}{ISO\ brightness\ of\ pile\ papers}$

		PACITY	- WHITE F	RINTING	PAPERS	[%]
	Base	2 pph	10 pph	20 pph	50 pph	100 pph
	91.4	98.0	97.5	96.2	93.6	92.7
	91.0	97.6	97.5	95.4	93.2	93.9
	89.7	99.6	96.6	96.5	94.9	94.1
	89.3	98.2	97.1	96.6	93.9	93.1
	89.9	98.7	97.6	96.1	93.4	94.8
	91.2	98.6	97.7	96.1	93.3	94.4
	91.9	98.4	97.0	96.7	94.1	91.9
	90.4	98.3	96.7	96.5	94.6	92.1
	89.0	98.7	97.6	95.9	94.3	92.8
	90.7	98.0	97.1	95.8	92.8	92.4
Average	90.5	98.4	97.2	96.2	93.8	93.2
Standard deviation	1.0	0.5	0.4	0.4	0.7	1.0
Coefficient of variance [%]	1.1	0.6	0.4	0.4	0.7	1.1

Appendix 7

Time till maximum penetration of white printing papers

	Penetration time max [s]					
	Base	2 pph	10 pph	20 pph	50 pph	100 pph
	0.739	0.074	0.075	0.116	0.226	0.239
	0.542	0.075	0.074	0.173	0.09	0.538
	0.538	0.075	0.074	0.075	0.074	0.074
		0.075			0.234	0.254
Average	0.61	0.07	0.07	0.12	0.16	0.28
Standard deviation	0.115	0.001	0.001	0.049	0.086	0.193
Coefficient of variance [%]	18.952	0.669	0.777	40.564	54.974	69.725

Appendix 8Cobb₆₀ value of white printing papers

	Cobb ₆₀ OF WHITE PRINTING PAPERS [g/m ²]							
	Base	Base 2 pph 10 pph 20 pph 50 pph 100						
	16.8	31.2	28.6	26.8	13.5	6.5		
	19.3	33.5	27.8	28.7	11.1	6.9		
	18.4	32.2	27.4	28.4	11.4	9.5		
		29.8			10.7	4		
Average	18.17	31.68	27.93	27.97	11.68	6.73		
Standard deviation	1.266	1.565	0.611	1.021	1.250	2.251		
Coefficient of variance [%]	6.970	4.941	2.187	3.652	10.707	33.479		