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Modified Egyptian talc as internal sizing agent for papermaking

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ABSTRACT

Mineral fillers have long been used in papermaking. The furnish of the writing and printing paper depends on using the fillers as internal or surface treatments. Talc, as an Egyptian filler material, was used as it is or after modification to be used as internal sizing for bleached rice straw pulp. Talc was modified chemically with phthalic anhydride and urea, as well as with using rosin size. Talc is chemically inert. The modification was carried out to change the nature of the native talc. The mechanical and optical properties for internal sizing papers were studied. The results indicated that modified talc with phthalic anhydride enhances the mechanical and optical properties for sized hand-sheets. It was clear that modification of the talc plays a role in improvement of the fiber–filler–fiber bond.

1. Introduction

Paper not only consists of cellulose fibers but also considerable amounts of other substances are added prior to sheet formation. It helps in improving some paper properties or implementing new properties. Paper is a bonded, more or less randomly, network of plant fibers, usually wood pulp fibers, making up an extremely complicated structure. In the paper making operation, a mat of fibers with a layered structure is formed on or between moving wires through which a water suspension of fibers is drained. In this process and during the subsequent pressing and drying of the sheet, it helps to develop fiber-to-fiber bonding in paper is a reflection of the bonded area between the fibers and the specific forces holding the fibers together.

Papermaking use fine mineral particles, i.e. "fillers", to achieve opacity, smoothness, and brightness goals. Another common goal of filler use is to decrease the net cost per mass of materials in paper. Mineral fillers have long been used in papermaking as internal or surface treatment. The term "internal sizing" is used by paper technology to describe the practice of adding chemicals to aqueous slurries that contain cellulosic fibers, so that the resulting paper is able to resist water or other fluids (Crouse & Wimer 1990; Davison 1975, 1986; Keavney & Kulick 1981; Reynolda, 1989; Eklund & Linström, 1991; Hodgson 1994; Hubbe 2005; Neimo 1999). Very small amounts of additives are able to overcome the inherent wettability of the cellulose and hemicellulose (Hansen & Bjöerkman 1998), the two main chemical components of ordinary paper.

In many paper grades, filler such as clay, calcium carbonate and titanium dioxide are added to increase opacity and brightness. The presence of fillers, however, prevents good fiber-to-fiber contact and thus reduces the paper strength, but other properties are improved rendering the paper useful to be used for special purposes (Al-Mehbad 2004; El-Shinnawy, Mobarak, Soliman, & El-Gendy 1997; Mobarak, El-Shinnawy, Soliman, & El-Gendy 1998; Sefain, Mobarak, Fadl, & Kassem 2006). Fillers have also an influence on the pore structure of paper. Some filler appears to be somewhat incompatible with certain sizing agents (Moyers 1992). To overcome such problems, it is sometimes recommended to cover up mineral surface with other materials before their addition to the paper machine system (Kurrle 1995).

Talc, which is hydrophobic filler, has numerous applications because of its chemical and thermal stabilities and lamellar morphology. Talc can be considered inorganic polymer based on two basic "monomer" structure – the silica tetrahedron and the magnesia octahedral. These minerals contain a continuous octahedral layer with the joined octahedra titted on a triangular side. This layer is bound on both sides by a continuous silica layer (Ciullo & Anderson 2002; Papirer, Balard, Baeza, & Clauss 1993). The talc is chemically inert, which led to poor fiber-to-filler-to-fiber bonding, thus our goal aims to modify the surface of the talc in order to enhance its use as sizing agent and thus improve the papermaking properties.

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2. Materials and methods

2.1. Materials

Commercial bleached rice straw pulp was kindly provided by The General Company for Paper Industry (RAKTA), Alexandria, Egypt, and was used as a source for the cellulosic raw material for the papermaking. Alpha-cellulose, hemicellulose, lignin and ash content were analyzed for the already bleached pulp. The results of the analysis are reported in Table 1.

On the other hand, commercial Egyptian talc was the source for the filler used as internal sizing before and after modification. The chemical analysis for the talc was carried out on Axios, Sequential WD_XRF, PANalytical 2005 instrument.

2.2. Methods

2.2.1. Modification of the talc

2.2.1.1. Modification of talc with phthalic anhydride and urea. A mixed sample made from mixing the dried urea with the dried phthalic anhydride in a mortar at equivalent weight in a 50 mL of distilled water. The mixture was heated at 170 °C in an oil bath under reflux for 6 h. At the end, the resulted precipitate was filtered, washed with distilled water then dried.

The crystals of phthalimide produced was mixed with talc and heated at 60 °C in a water bath for 24 h with contentious stirring. At the end, the modified talc was ground and used as internal sizing for papermaking.

2.2.1.2. Addition of rosin size with talc. Rosin size solution, 2.5% based on the dry weight fiber, was used in the presence of 5% native talc, based on the dry weight fiber, during papermaking. Alum was used to precipitate the rosin size at pH around 4.5. The mixture was made in the head box, and the paper-sheets were then made.

2.2.2. Sheet making

The paper sheets were prepared according to the (SCA) standard, by using the SCA-model sheet former (AB Lorenzen and Wetter). In the apparatus, circular sheets of 165-mm diameter and a 214 cm^2 surface area were formed by using 1.6 g oven dry pulp. The sheet was then pressed for 4 min by using hydraulic press. Sheet samples were dried in drum for 2 h. Finally, the sheets were placed for conditioning in polyethylene bags.

Native talc and modified talc were added in a 5%, based on the dry weight of the fiber, to the bleached rice straw pulp in the head box, before the sheet formation. After mixing, the sheets were prepared as described according to the SCA standard.

2.2.3. Mechanical and optical test of hand sheets

2.2.3.1. Mechanical tests. After conditioning, the hand sheets, filled and unfilled, were weighed, and divided into suitable pieces for the physical tests. In accordance with the standard methods, the tensile and tearing strength of the sheets were measured and then the percent increase of both the breaking length and the tear factor were calculated.

Table 1
Analysis, in percent (%), of the commercial already bleached rice straw pulp

Alpha-cellulose	62.12
Hemicellulose	17.63
Lignin	5.3
Ash	13.82

2.2.3.2. Optical properties

2.2.3.2.1. Brightness Rα. The amount of reflectance of pads of so many sheets of paper that no change in reflectance occurs when a backing is used, is called *Rα*. This intensity of light designates the brightness of paper compared with the intensity of light reflected by a standard white body at the same wavelength. The apparatus used in this work for measuring the brightness was a Hunter Lab Colour/Difference Meter D25-2.

2.2.3.2.2. Opacity Ro. When a single paper sheet is backed by a black body, the amount of reflected light would not be changed if the single paper sheet does not permit the passage of light through its thickness, i.e. the paper is completely nontransparent. However normal writing and printing paper allows the passage of a certain percentage of the incident light. Therefore, when the single paper sheet is packed by a black body, the reflectance is less and is designated *Ro*, but brightness is designated *Rα*.

The ratio *Ro*:*Rα* is called the printing opacity. The Hunter Lab Colour/Difference Meter D25-2 is used for measuring the opacity.

2.2.4. Determination of pigment retention

The simplest and most accurate method of calculating pigment retention is to determine the ash content of sample stock taken from the beater and the sample finished paper taken from the paper machine. After the ash figures have been converted to filler content, the weight of filler appearing in the paper can be divided by the weight of filler in the stock at the beater to give the percentage retention. The retention value obtained in this way indicates the amount of filler lost in the papermaking operation as a whole.

The percent of the retention of the filler can be calculated according to the following equation:

$$\%\ \text{Retention} = \frac{\text{weight of the ash}}{\text{weight of the filler added}} \times 100$$

2.2.5. Sizing test: (Sizability)

An indicator is prepared by mixing 1 part methyl violet dye with 45 parts sugar and 5 parts soluble starch. All ingredients are to be completely dry and finely powdered when mixed and are to be stored over calcium chloride pending use. The nearly colorless dry indicator becomes deep violet in contact with water.

The test is performed by sealing the four edges of the test specimen with wax, sprinkling a thin, uniform layer of indicator upon the surface, and then floating the specimen, indicator side up, upon a vessel of water. The time interval from the instant of contact of the test specimen with water until the rate of change in the color of the indicator is at maximum.

2.2.6. Scanning electron microscope

Scanning electron microscope (SEM) for the prepared handmade sheet was investigated using JEOL JXA-840A electron probe microanalyzer.

3. Results and discussion

Talc is widely used due to its properties such as chemical inertness, softness, high thermal conductivity and low electrical conductivity, adsorption properties, etc. The main industrial applications of talc are in the paper, cosmetics, paints, polymers, ceramics, refractories and pharmaceuticals (Madson 1967; Martens 1974).

At the chemical point of view, talc is a hydrophobic and organophilic matter. It is a hydrated magnesium sheet silicate with the chemical formula $Mg_3Si_4O_{10}(OH)_2$ (Ciullo & Anderson 2002). The analytical composition of the commercial talc used in this work shows 25.39% MgO and 65.76% SiO_2. Talc's crystalline structure consists of a MgO/MgOH octahedral layer, which lies between two SiO tetrahedral layers (Ciullo & Anderson 2002). As observed by the SEM, Fig. 1, the crystal habit of talc corresponds to flattened tabular crystals with a hexagonal cross-section.

Native talc was added to the commercial bleached rice straw pulp in an amount of 5% based on the dry weight of the pulp. The prepared sheets were dried, and the optical and mechanical properties were investigated and expressed by brightness, opacity, breaking length, and tear factor.

The improvements in percentages in mechanical properties are given in Table 2. From Table 2, it is obvious that the breaking length decreased on addition of 5% native talc. This decrease in the breaking length is attributed to the chemical behaviour of the talc. The talc is chemically inert, which led to poor fiber-to-talc-to-fiber bonding and hence a decrease in the breaking length obtained.

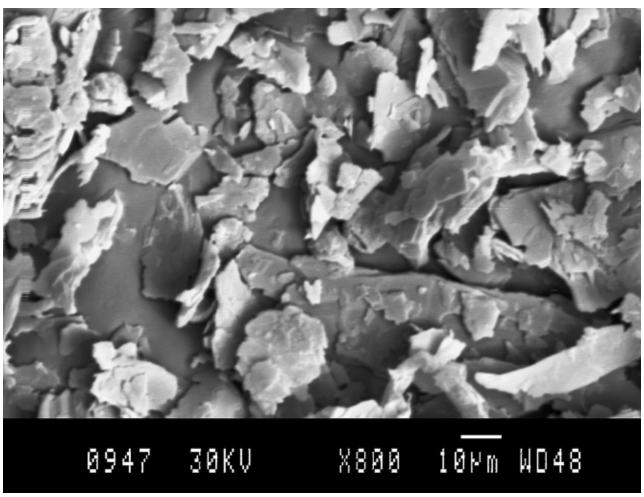


Fig. 1. SEM for native Egyptian talc.

Examination of scanning electron micrographs from blank hand-made sheet and that with 5% talc (Fig. 2a and b) shows a web like structure with fiber-fiber bond for the blank sheet (Fig. 2a) and in presence of the talc, Fig. 2b, it is noticed that the talc filled the space between the web structure with poor fiber-to-talc-to-fiber bond.

Moreover, the addition of 2.5% of rosin size in the head box during the sheet formation results in an enhancement on the tear factor and the sizability (Table 2). Generally, the rosin-type sizing agents are often called "acidic sizes". They tend to be most efficient in pH ranges about 4–6. The rosin requires use of mordant, such as alum, to fix the hydrophobic molecules to the paper surface (Marton 1989; Strazdins 1977; Strazdins 1984), it precipitated onto the fiber surfaces by the addition of the alum at the wet end of the paper machine (Back & Steenberg 1951). Fig. 3 illustrates the SEM of the hand-made sheet in the presence of the talc and rosin size. It can be seen that an agglomerated film is formed between the cellulosic fibers of the hand-sheet.

It is known that the rosin size includes abietic acid (Lee, Hubbe, & Saka 2006; Strazdins 1989, chap. 16) which is a multi-ring compound. It is generally hydrophobic, except that it contains a carboxylic acid group. The reaction between the rosin and the alum has been shown by Davison (1975) and Eklund and Linström (1991) to yield mixture of aluminum diresinate and free resin. In the presence of the talc, which is a hydrated magnesium silicate, the magnesium ion can cause premature agglomeration of the rosin size. This agglomeration may cause the carboxyl groups on rosin become blocked, no longer able to participate in interactions with the alum as a mordant material and thus the rosin size remained in an untreated form with the paper sheet, even after the paper was dried. This can explain the decrease in the breaking length because of the poor fiber-to-filler-to-fiber bond.

On the other hand, the addition of modified talc with the mixture of phthalic anhydride and urea results in an enhancement of the mechanical properties as well as the sizability (Table 2). The SEM of the resulted hand-sheets (Fig. 4) showed a plasticized mat structure formed on the cellulosic fibers that can be the reason for a good fiber-to-filler-to-fiber bond.

Table 2
Optical and mechanical properties of bleached rice straw hand-made sheets: (a) blank sheet; (b) addition of native talc; (c) addition of talc and rosin size; and (d) addition of amphiphilic modified talc

Samples	Mechanical properties		Optical properties			
	% Increase in breaking length	% Increase in tear factor	Brightness (%)	Opacity (%)	Sizability (s)	Pigment retention (%)
(a) Blank	–	–	65.80	98.00	90	–
(b) 5% Talc	−7.11	42.89	68.80	98.41	104	65.5
(c) 5% Talc and 2.5% rosin size	−4.66	188.46	65.75	98.00	210	82.7
(d) 5% Amphiphilic modified talc	39.11	100.00	66.05	98.75	176	39.4

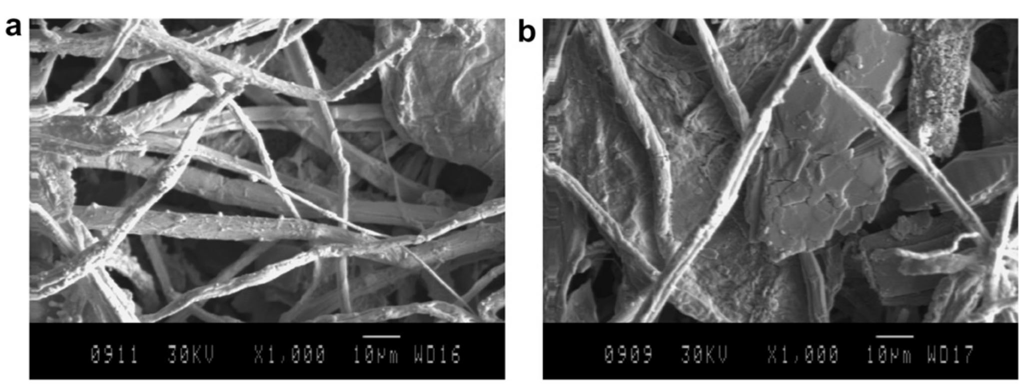


Fig. 2. SEM for (a) blank sheet, and (b) with the addition of 5% of native talc.

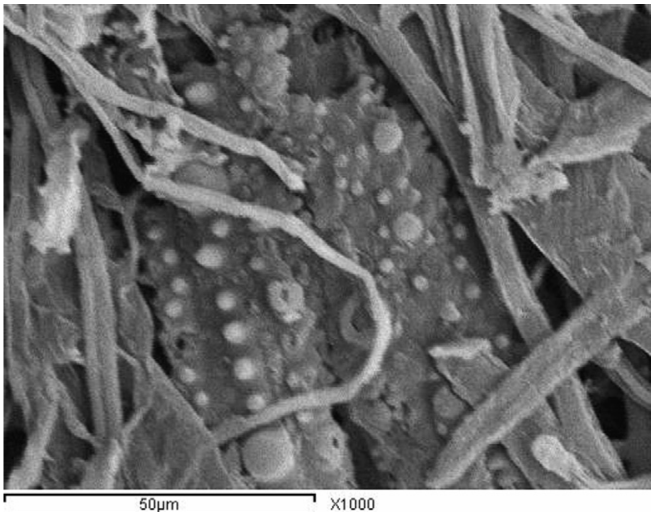


Fig. 3. SEM for hand-made sheet in the presence of talc and rosin size.

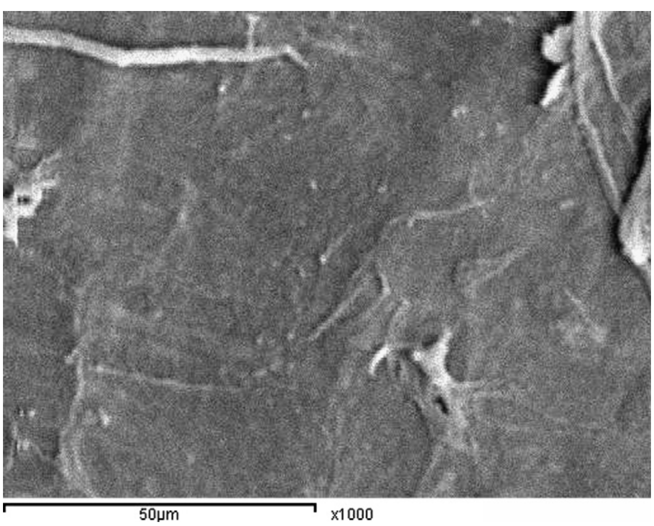
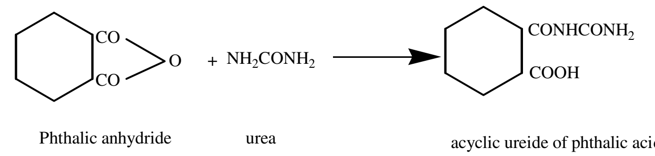
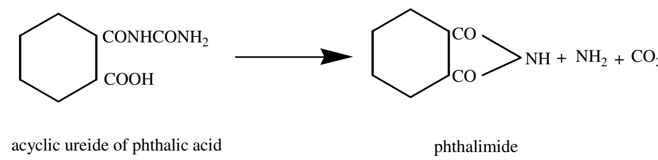


Fig. 4. SEM for hand-made sheet in the presence of the amphiphilic modified talc.

It is already known (Smith & Cavallito 1939) that by heating the mixed sample containing equimolecular quantities of phthalic anhydride and urea at 120–126 °C the additive reaction is carried out and the acyclic ureide of phthalic acid is produced.



Increasing the temperature over 150 °C, phthalimide can be formed by the decomposition of the ureide of the phthalic acid (Smith & Cavallito 1939).



The modified talc with the phthalimide can led to amphiphilic copolymer which can form a bond between the NH group of the modified talc and the OH group of the cellulosic fiber to result in a good fiber-to-filler-to-fiber bond which increases the mechanical properties of the produced paper.

The higher of the sizability, i.e., the reduce in the water penetration can be due to the formation of the plasticized mat over the cellulosic fiber. This can be explained by the rearrangement of the produced amphiphilic modified talc upon drying of the paper sheet, such that more hydrophobic groups end up facing the air phase and more hydrophilic groups facing the fiber surface forming a bond with the cellulosic fiber.

As illustrated in Fig. 5, it would be expected that water-hating groups would tend to orient themselves facing outwards from the paper surface during the final stages of drying, thus decreasing the interfacial free energy of the system (Garnier, Duskova-Smrckova, Vyhnalkova, van de Ven, & Revol 2000).

It is generally agreed that resistance to the penetration of water requires a reduction in the free energy of paper's surface (Irvine, Aston, & Berg 1999; Krueger & Hodgson 1995). Aqueous fluids spread and penetrate with relative ease in the case of bare cellu-

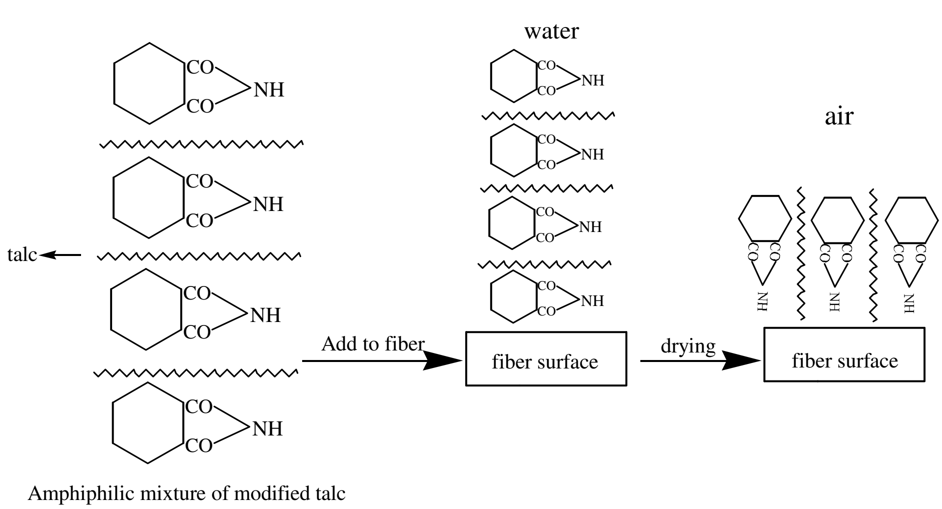


Fig. 5. Concept of rearrangement upon drying of amphiphilic modified talc.

losic surfaces, due to the ability of water to form hydrogen bonds with the surface hydroxyl groups of the polysaccharide-rich material. Hubbe (2006) has mentioned that the relatively high energy of interaction results in relatively low contact angles of water with cellulosic materials, where, by convention, the angle of contact is drawn through the liquid phase. By contrast, when a drop of water is placed onto a flat, non-wetting plastic surface, the angle of contact, by definition, is greater than 90 degrees. Thus, the internal sizing of paper can be envisioned as a way to transform the paper surface from a relatively high-energy state, rich in groups capable of hydrogen bonding, to a modified state in which the free energy of the surface is reduced.

4. Conclusions

The results indicated that modified talc with phthalic anhydride give higher mechanical properties and higher sizability when used as internal sizing agent for paper making compared to the native talc. Changing the chemical nature of the native talc by modification to form amphiphilic copolymer resulted in higher mechanical and optical properties due to the nature of the new product. On the other hand, the addition of the rosin size with the talc results in a decrease in the breaking length due to the presence of the magnesium ion of the talc which tends to agglomerate the rosin size and thus results in a poor bond with the cellulosic fibers.

References

Al-Mehbad, N. Y. (2004). Improving paper properties. *Polymer-Plastics Technology and Engineering, 43*(3), 963–979.

Back, E., & Steenberg, B. (1951). Isolation and properties of aluminum di- and mono-abietate. *Svensk Papperstidn, 54*, 510–516.

Ciullo, P. A., & Anderson, J. (2002). Industrial talc. *Journal of Coatings Technology, 74*(11), 15–19.

Crouse, B., & Wimer, D. G. (1990). *Alkaline sizing: An overview*. *TAPPI neutral/alkaline short course notes*. Atlanta: TAPPI Press.

Davison, R. W. (1975). The sizing of paper. *Tappi, 58*(3), 48–57.

Davison, R. W. (1986). A general mechanism of internal sizing. *Procedure TAPPI papermakers conference (pp. 17–17). Atlanta: TAPPI Press.*

Eklund, D., & Linström, T. (1991). *Paper chemistry, an introduction. Grankulla.* Finland: DT Paper Science Publisher.

El-Shinnawy, N., Mobarak, F., Soliman, A., & El-Gendy, A. (1997). Effect of oxidized starch and urea-formaldehyde as wet-end additives in Egyptian bagasse based paper. *Journal of Scientific and Industrial Research, 56*(1), 35–38.

Garnier, G., Duskova-Smrckova, M., Vyhnalkova, R., van de Ven, T. G. M., & Revol, J.-F. (2000). Association in solution and adsorption at an air–water interface of alternating copolymers of maleic anhydride and styrene. *Langmuir, 16*(8), 3357–3763.

Keavney, T. J., & Kulick, R.-J. (1981). Internal sizing (Ch. 13.. In J. P. Casey (Ed.). *Pulp and paper chemistry and chemical technology* (Vol. 3, pp. 1547–1592). New York: Wiley-Interscience.

Krueger, J. J., & Hodgson, K. T. (1995). The relationship between single fiber contact angle and sizing performance. *Tappi Journal, 78*(2), 154–161.

Kurrle, F. L. (1995). Process for enhancing sizing efficiency in filled papers. *U.S. Patent, Pat. No. 5,411,639.*

Hansen, C. M., & Bjöerkman, A. (1998). The ultrastructure of wood from a solubility parameter point of view. *Holzforschung, 52*(4), 335–344.

Hodgson, K. T. (1994). A review of paper sizing using alkyl ketene dimmer versus alkenyl succinic anhydride. *Appita, 47*(5), 402–406.

Hubbe, M. A. (2005). Acidic and alkaline sizings for printing, writing, and drawing papers. *The Book and Paper Group Annual, 23*, 139–151.

Hubbe, M. A. (2006). Paper's resistance to wetting – A review of internal sizing chemicals and their effects. *BioResources, 2*(1), 106–145.

Irvine, J. A., Aston, D. E., & Berg, J. C. (1999). The use of atomic force microscopy to measure the adhesive properties of size and unsized papers. *Tappi Journal, 82*(5), 172–174.

Lee, S. Y., Hubbe, M. A., & Saka, S. (2006). Prospects for biodiesel as a byproduct of wood pulping – A review. *BioResources, 1*(1), 150–171.

Madson, W. -H. (1967). *White hidding and extender pigments (Unit 7). Federation of Societies for Paint Technology.*

Martens, C. R. (1974). In E. Ropbert (Ed.), *Technology of paints. Varnishes, and Lacequers* (pp. 344). Melbourne, F.L.: Krieger Publishing Co..

Marton, J. (1989). Mechanistics differences between acid and soap sizing. *Nardic Pulp and Paper Research Journal, 4*(2), 77–80.

Mobarak, F., El-Shinnawy, N. A., Soliman, A. A. A., & El-Gendy, A. A. (1998). Effect of some chemical treatments of upgraded Egyptian kaolin on its retention by bagasse pulp. *Journal of Scientific and Industrial Research, 57*(6), 316–323.

Moyers, B. M. (1992). Diagnostic sizing loss problem solving in alkaline systems. *Tappi Journal, 94*(1), 111–115.

Neimo, L. (1999). Internal sizing of paper. In L. Neimo (Ed.), *Papermaking Chemistry* (pp. 151–203). Fapet Oy.

Papirer, E., Balard, H., Baeza, R., & Clauss, F. (1993). Chlorination of talc surface. *European Polymer Journal, 29*(4), 555–558.

Reynolda, W. F. (Ed.). (1989). *The sizing of paper, 2nd ed. Berlin: Springer.*

Sefain, M. Z., Mobarak, F., Fadl, M. H., & Kassem, N. F. (2006). Improvement of paper properties part II: Addition of kaolin and starch to bagasse paper sheets treated with gelatin-hexamine. *IPPTA, 18*(1), 33–37.

Smith, C. S., & Cavallito, C. J. (1939). A study of some derivatives of phthalyl urea. *Journal of the American Chemical Society, 61*(8), 2218–2221.

Strazdins, E. (1977). Mechanistic aspects of rosin sizing. *Tappi Journal, 60*(10), 102–105.

Strazdins, E. (1984). Critical phenomena in rosin sizing. *Tappi Journal, 67*(4), 110–113.

Strazdins, E. (1989). Paper sizes and sizing. In D. F. Zinkel & J. Russell (Eds.), Naval stores: Production,chemistry, utilization (pp. 575–624). New York: Pulp Chem. Assoc.