

Starch granules spot-coated with aluminum silicate particles and their use as fillers for papermaking

K. Koivunen · H. Alatalo · P. Silenius ·
H. Paulapuro

Received: 2 October 2009 / Accepted: 13 February 2010 / Published online: 2 March 2010
© Springer Science+Business Media, LLC 2010

Abstract Mineral fillers are among the most important raw materials of paper. In papermaking, a filler is typically mixed as such with the fibrous stock prior to the forming section where it, together with the fibers and fines, forms a paper web with heterogeneous three-dimensional composite structure. The filler is eventually located both in the paper pores and between adjacent fibers. When light interacts with a multitude of solid-air interfaces occurring in such a structure, complicated light scattering effects take place. These effects are essential for appearance development, *viz.* brightness and opacity. Fillers contribute to these effects by increasing the number of such interfaces. Many fillers also cost significantly less than fibers. Therefore, it is advantageous to introduce as much filler as possible. It is also well known, however, that filler prevents formation of hydrogen bonding and is hence detrimental for strength development. In addition, the legislation of European Union favors increasing recovery of paper and packaging products, e.g., for energy production. However, as a side

product of paper waste incineration, significant amounts of ash is formed. Hence it would be advantageous to replace inorganic fillers with combustible organic materials. We have fabricated a novel aluminum silicate spot-coated starch-based filler. The results indicate that when silicate is introduced in paper on the surface of starch granules benefits in light scattering and strength development can be achieved.

Introduction

As an essential raw material of paper, the purpose of fillers is to replace expensive fiber, provide surface for effective light scattering, and usually also to enhance printing properties. As light interacts with paper, part of it travels through the surface and propagates into the heterogeneous three-dimensional network with multitude of solid-air interfaces on which reflections and refractions beyond measure take place. These light scattering effects have a fundamental importance for the development of appearance and printability of paper. Filler pigments increase light scattering through two mechanisms, *i.e.*, by increasing the specific surface area of the matrix, and by preventing bonding between fibers [1].

Hence, paper optical properties are improved by filler addition at the expense of paper strength. This occurs, first of all, due to the replacement of fibers by filler. Secondly, as the fillers retain more or less together with the fibers, they are finally deposited, not only in the empty spaces of the fiber matrix, but also between the fiber surfaces [2], preventing the bond formation as the fibers are pulled together by Campbell forces at the final stages of web consolidation.

K. Koivunen (✉) · H. Paulapuro
School of Science and Technology, Department of Forest
Products Technology, Aalto University, P.O. Box 16300,
00076 Aalto, Finland
e-mail: kimmo.koivunen@tkk.fi

H. Alatalo
Department of Chemical Technology, Lappeenranta University
of Technology, PL 20, 53851 Lappeenranta, Finland

P. Silenius
Technology Centre Kirkniemi, M-real Corporation, 08800
Kirkniemi, Finland

Present Address:

P. Silenius
Kemira Oyj, P.O. Box 44, 02271 Espoo, Finland

Therefore, a way to obtain indication about papermaking potential of a specific filler is to plot the light scattering coefficient of the filled sheet as a function of strength [3].

Filler type and size affect the degree of strength reduction. Deterioration of strength is in particular caused by small particles [4–6]. In contrast, coarse particles with narrow size distribution yield comparatively high strength. Degree of flocculation affects as well. Holm and Manner [7] have shown that by preflocculation of filler into larger agglomerates strength reduction is more moderate than by conventional filler addition. Small particle size, around half wavelength of light, would be, however, optimal for the light scattering.

Besides utilizing preflocculation, the strength reduction can be restrained by some additional means. Several approaches are used in improving the dry strength of paper with starch. Starch is typically added in soluble form in the stock or applied on paper web at the size press. To avoid operational problems at PM the dosage of stock starch is typically limited. Starch can also be introduced in uncooked form [8]. Surfaces of, e.g., clay filler have also been coated with starch to diminish the negative strength effects [9].

Nowadays vast amounts of inorganic material are separated from fibers in deinking lines. Deinking sludge formed for example in flotation stage of deinking plant can contain over 50% inorganic material such as clay and calcium carbonate [10]. Deinking sludge is dewatered and used for landfill, used in industrial purposes, or combusted [11]. The European Union has set goals for increased recovery. However, in incineration of paper waste or sludge, high amounts of ash are formed. New solutions are needed to avoid the problems and costs related to the generation and disposal of ash.

Efforts have been made to develop organic pigments, such as plastic pigments, urea–formaldehyde pigments, and various modified starch-based pigments [6, 12–14].

We have used starch granules as such. The size distribution of starch granules significantly depends on the originating plant. Considering paper filler applications, starch particles are relatively large. For instance, potato and corn starches display particle sizes 10–100 μm and 5–25 μm , respectively [15], whereas the particles of traditional fillers are typically no larger than 3 μm . Therefore, the light scattering potential of native starch granules is naturally far below the level provided by conventional fillers or optimized granules. Our approach was to optimize the surface with other material, and leave the carrier granules themselves unaffected. In the light of previous knowledge [4–6] the high particle size of the granules in our case, around 30 μm , was considered beneficial for paper strength.

Various surface coating approaches have been introduced to improve the light scattering potential of pigments.

The light scattering from (calcium carbonate) particles can be increased by coating the granules with a thin continuous layer of higher refractive index (RI) material [16]. It is known that through a thin, continuous layer (<200 nm) propagation of light is not significantly affected. Instead, fine particles introduced at an optimum distances on the filler surface work better. This is, for instance, because the fine particles on the host material surface provide increased interparticle spacing. Decreased amount of contact points between the host filler particles is beneficial in the development of the light scattering effects because solid–solid contacts are replaced by solid–air interfaces displaying higher refractive index contrasts. Furthermore, when compared with continuous layers, less material is needed in such a spot coating approach. Koivunen et al. [17] have earlier suggested zinc based nanostructuring as means to increase the light scattering potential of precipitated calcium carbonate (PCC). In the present study the authors deposited aluminum silicate particles on the surfaces of the starch granules. Patent application covering starch–silicon composites has been earlier filed by the authors [18]. Detailed descriptions on fabrication of other composite pigments containing silicate can be found in patent literature [19, 20].

Materials and methods

Aluminum silicate particles were deposited on native or anionic starch granules (Raisio Group) reacting sodium silicate (Zeopol, Huber Engineered Materials) with aluminum sulphate (2331350, Kemira Oyj) in 4.0 dm³ reactor with the presence of the granules. Three different spot-coated starch samples were fabricated.

First, some alum, starch granules, and some magnesium hydroxide were dispersed in deionized water and added in the reactor. Aluminum silicate was then deposited on the starch granules in the second stage by adding sodium silicate and alum dissolved in deionized water. Duration of the addition depended on the test point in question. The pH was adjusted to 7. The product was then filtered and analyzed. Sample 1 was also washed after filtration. The fabrication conditions are listed in Table 1.

Size distributions of the spot-coated granules were measured with Coulter LS 130. The spot-coated surfaces were analyzed with SEM.

Dried chemical pulp, consisting of 70 wt% birch and 30 wt% pine, delivered by Finnish and Swedish pulp mills, respectively, was soaked in water and beaten according to the standard SCAN-C 25:76 until a 50 Nm/g tensile strength index for 60 g/m² sheets was achieved without fillers. The stock was then diluted to 0.3% consistency for sheet preparation.

Table 1 The spot coating conditions of the starch granules

	Sample		
	1	2	3
<i>Initial solution</i>			
Alum (g)	6.6	6.6	6.6
Starch (g)	31	31	31
Starch type	Native	Anionic	Anionic
Mg(OH) ₂ (g)	2	1:1	1
Water (g)	1000	1000	1000
T (°C)	40	40	40
<i>Silicate deposition</i>			
Silicate (g)	414	414	414
Alum (g)	67.5	67.4	67.4
Water (g)	389	389	389
Duration (min)	10	5	9

The spot-coated granules with the most beneficial particle size distributions regarding interaction with light were used as a filler in handsheet experiments. 60 g/m² handsheets were prepared by applying the standard SCAN-C 26:76. Dilute filler was dosed into the sheet mold after the stock addition. After forming a sheet, two blotting boards were set onto it, and the sheet was then was couched with a couch roll. The outer blotting board was removed, and the sheet was placed together with the blotting board attached to the sheet, on a drying plate. Wet pressing of the sheets was done by mounting a stack of the sheets, containing the drying plates and the blotting boards, into the press. The stack was pressed under (400 ± 10) kPa in two stages. A commercial aluminum silicate filler was used as reference. Silicate content targets were 6% and 14%, relative to the weight of the base paper, both when introduced through conventional addition directly to the stock, and when deposited first on the starch granules.

Laboratory handsheets are typically dried in 23 or 60 °C depending on whether drying plates are used or not, respectively. A simple test was performed to obtain an indication of the starch granule ability to stand drying in elevated temperature. The shape of starch particles may, in the presence of water, change as the polymer chains start to dissolve in the gelatinization temperature [15]. Part of the wet pressed, moist sheets were heated up in a fan drier specifically constructed for the experiment. Each sheet was wrapped into an aluminum foil with its drying plate. A sensor of an electronic thermometer was set into the packages, between the foil and the sheet. The package was further placed on a drying sheet metal, used in conventional plate drying of handsheets, and the fabric of the drying sheet metal was strained over the package. The entire set was then placed into the heated chamber (90 °C)

of the fan drier. The heat treatment duration was 10 min. Subsequently, the plate drying in standard conditions (23 °C, 50% RH) was completed. Finally the sheets were analyzed with standard paper testing methods.

Results

The particle size distributions of the spot-coated starch fillers are presented in Fig. 1. The mean particle size of the coated granules is around 30 μm, order of magnitude

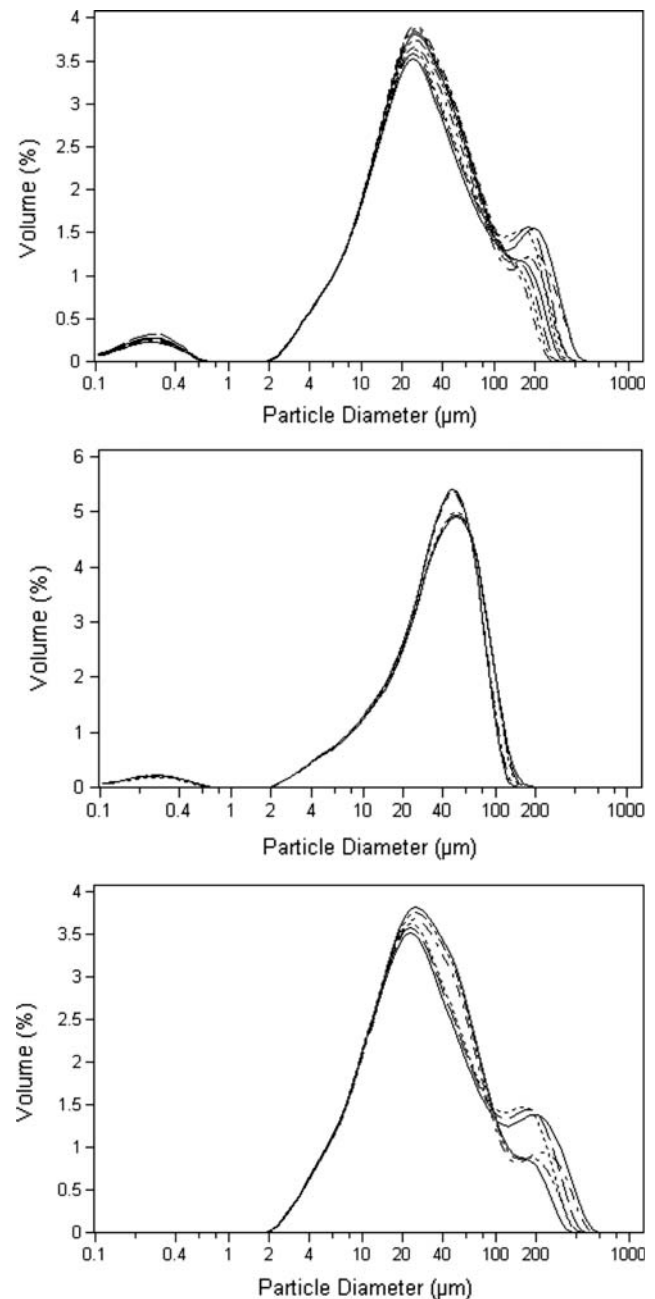
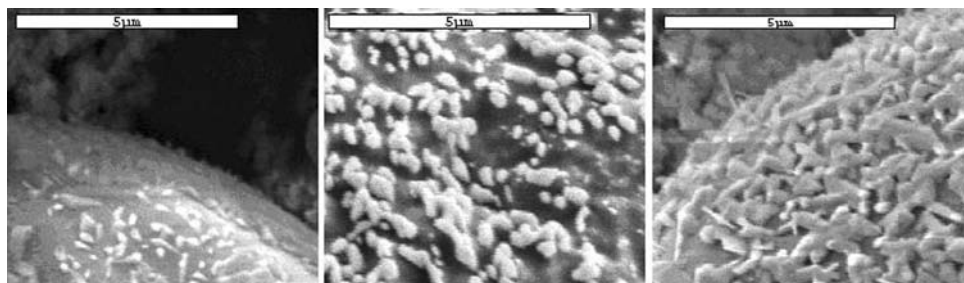


Fig. 1 Differential particle size distributions of spot coated starch granules. Sample 1 (*top*), 2 (*middle*), and 3 (*bottom*)

Fig. 2 Spot structures observed in samples 1 (left), 2 (middle), and 3 (right)



roughly tenfold with regard to the size exhibited by conventional fillers. Significantly smaller particles are usually preferred to generate effective light scattering. In contrast to the starch fillers, the reference filler exhibits more typical particle size, around 5 μm, as suggested by Fig. 3.

However, the fillers must be examined in detail to obtain more information on their light scattering potential. Figure 2 presents micrographs of the surface of aluminum silicate-coated starch granules. The figures suggest an evenly dispersed introduction of fine silicate particles on the large starch granules. Based on the micrographs, the estimated size of the silicate particles varies in the range of 50–500 nm which is around the optimum size. Figure 2 also suggests that the silicate particles have been usually deposited at an optimum spacing (≥ 200 nm) on the starch granules, which is beneficial for the light interaction as well.

The reference aluminum silicate filler is presented in Fig. 3. The filler consists of closely aggregated fine spherical aluminum silicate particles, building up irregularly shaped highly porous larger pigment structures. The size of the fine particles is around 100–200 nm.

In contrast to the silicate-coated starch fillers, in the case of the reference the fine particles are arranged in relatively

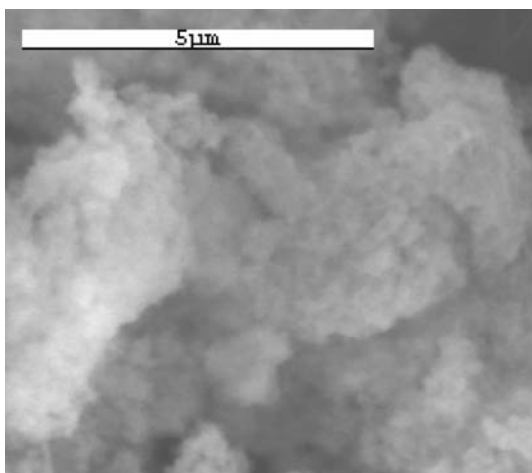


Fig. 3 Aluminum silicate-based reference filler

densely packed configuration displaying less spacing and probably more contact points to the surrounding particles. Due to the lack of refractive index (RI) differences between the particles, however, light scattering is not as effectively

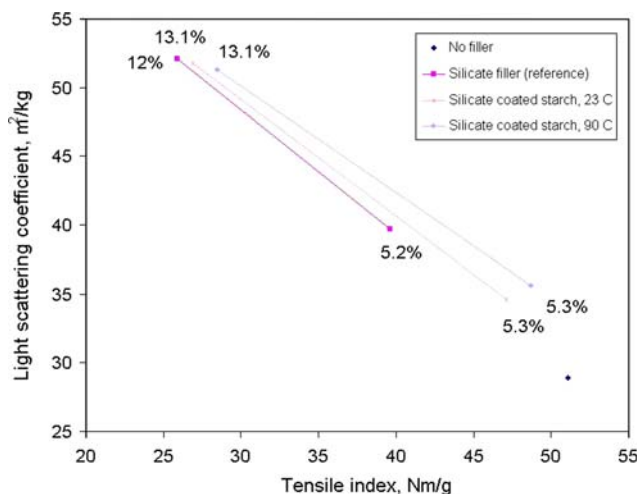


Fig. 4 Light scattering coefficient against tensile index in different Al-silicate contents. Sample 2. Drying temperature is marked in the legend

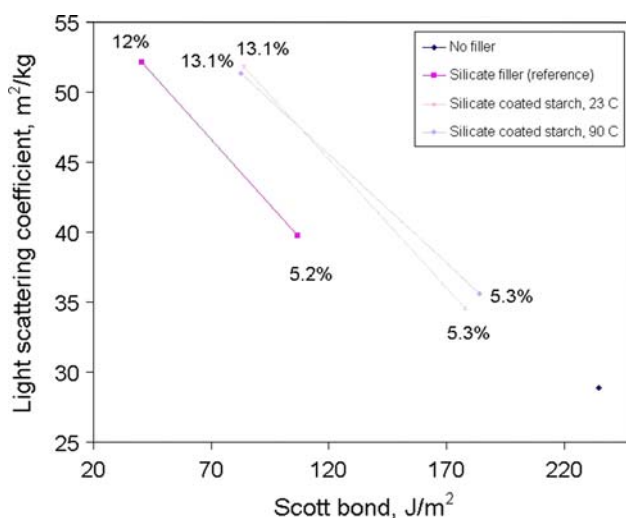
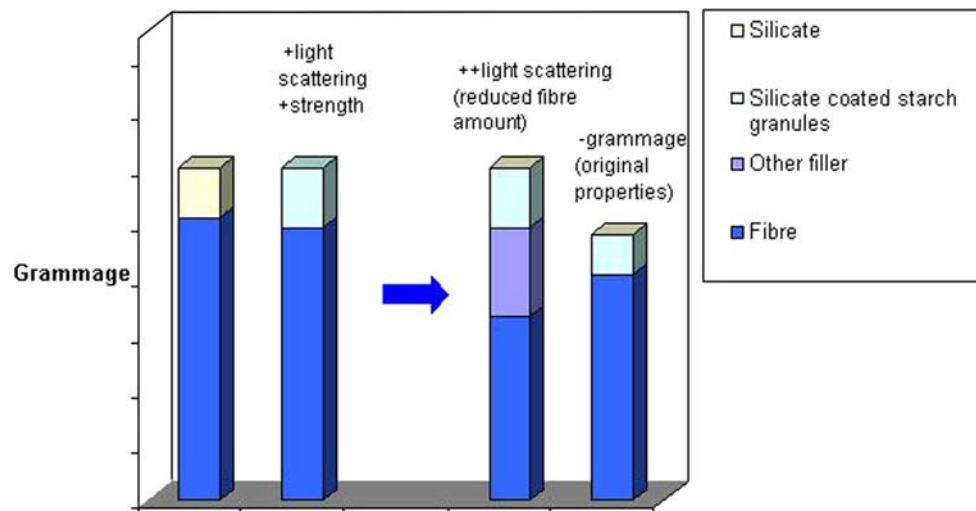


Fig. 5 Light scattering coefficient against Scott bond in different Al-silicate contents. Sample 2. Drying temperature is marked in the legend

Fig. 6 Schematic figure of grammage reduction and fiber replacement enabled by Al-silicate spot-coated starch granule filler



generated in the absence of suitable interparticle spacing, i.e., porosity. In optical sense, interparticle spacing, displaying no less than 200 nm distance between the particles, is most beneficial.

Paper technical properties of sample 2 are presented in Figs. 4, 5. It should be noted that the percentages marked in the figures describe the aluminum silicate content in the sheet, excluding the weight of the starch granules. The results suggest significant benefits in light scattering coefficient–strength property combinations when aluminum silicate is introduced in paper on the starch particle surfaces instead of through conventional manner. This is suggested to be due to the synergy provided by the fine dispersed silicate and the host starch granules. Being attached to the host particles, the silicate particles provide effective light scattering, but do not excessively disrupt the fiber network which would probably be the case if introduced in conventional way. The restrained deterioration of strength is achieved due to large particle size provided by the starch host granules. The benefit is further confirmed in Scott bond (Fig. 5).

The drying temperature of the handsheets did not have significant effect on the results. This suggests the ability of the starch particles to withstand the drying conditions examined.

For the papermaker, as illustrated in Fig. 6, the benefit of using silicate-coated starch instead of silicate introduced as such in the fibrous stock can be realized through improved appearance, reduced grammage or increased utilization of renewable material, depending on the application. This can be controlled by the silicate coverage of the surface. The results illustrate clearly that not only filler content, but also the way the filler is introduced, significantly affect the resulting functional behavior of paper.

However, before being able to extend the use of the spot-coated starch fillers to industrial scale, some usability

issues are to be considered. These are, for instance, biological and runnability aspects, including possible starch gelatinization during drying, and its consequent effects on the broke handling, and deposit formation.

Printability provided by the novel fillers also needs more research. Traditional Al-silicate fillers provide superior printability.

Finally, economic feasibility must be further evaluated.

Conclusions

Our results suggest that aluminum silicate filler, when deposited as fine dispersed particles on large starch granules, can provide an improved combination of light scattering and strength with regard to the same mass of the Al-silicate filler introduced in paper by the conventional way. Silicate-coated starch granules could help to reduce fiber costs through an increased filler content or reduced grammage. Starch granules could also be utilized to increase the amount of renewable material in paper. This would further improve the usability of recovered paper and sludge in energy production of the future. However, some usability aspects of the novel starch granule fillers should be further assessed.

Acknowledgements The financier, M-real Corporation, is gratefully acknowledged. Thanks are also due to Mr. Olli Ruottinen for the handsheet preparation.

References

1. Hemstock GA (1962) *Tappi* 45(2):158A
2. Weigl J, Zeuner M, Baumgarten HL (1981) *Papier* 35(10A):V46
3. Alince B (1989) In: Baker CF (ed) *Transactions of the fundamental research symposium, vol 1. Mechanical Engineering Publications, Cambridge, pp 495–510*

4. Adams JM (1993) *Clay Miner* 28:509
5. Fairchild GH (1992) *Tappi J* 75(8):85
6. Krogerus B (1998) In: Neimo L (ed) *Papermaking chemistry*. Fapet Oy, Jyväskylä
7. Holm M, Manner H (2001) In: 28th DITP International annual symposium. Technical, technological and biological processes for the improvement of production, productivity, quality and ecology in papermaking. Bled, Slovenia, 14–16 Nov 2001, pp 167–170
8. Johnston H (2002) *TAPPSA J* 30
9. Zhao Y, Kim D, White D, Deng Y, Patterson T, Jones P, Turner E, Ragauskas AJ (2008) *Tappi J* 7(3):3
10. Hanecker E (1994) *Alternative Verwertung von Reststoffen—ausser thermische Nutzung—getrennt nach Fasern und Füllstoffen*, INDEGE Report 2892 PTS, Papiertechnische Stiftung, Munich
11. Hamm U (1998) In: Götsching L, Pakarinen H (ed) *Recycled fiber and deinking*, Fapet Oy, Jyväskylä
12. Heiser EJ, Shand A (1973) *Tappi* 56(2):101
13. Gruber E, Bothor R, Dintelmann T (1998) In: *EUCEPA symposium 1998—chemistry in papermaking*, Florence, Italy, 12–14 Oct 1998, pp 379–391
14. Varjos P, Mikkonen H, Kataja K, Kuutti L, Luukkanen S, Peltonen S, Qvintus-Leino P (2004) In: *PulPaper 2004: coating*, Helsinki, Finland, 1–3 June 2004, pp 131–134
15. Ketola H, Andersson T (1998) In: Neimo L (ed) *Papermaking chemistry*, Fapet Oy, Jyväskylä
16. Lattaud K, Vilminot S, Hirlimann C, Parant H, Schoelkopf J, Gane P (2006) *Solid State Sci* 8(10):1222
17. Koivunen K, Niskanen I, Peiponen K-E, Paulapuro H (2009) *J Mater Sci* 44(2):477. doi:[10.1007/s10853-008-3095-ys](https://doi.org/10.1007/s10853-008-3095-ys)
18. FI120318. *Composites of Starch Containing Silicon, Method for the Production Thereof, and Use for Making Paper and Board*. Applicant: M-real Corporation. Inventors: Silenius, P., Koivunen, K., Alatalo, H
19. WO0192422. *Composite Precipitated Calcium Carbonate/Silicon Compound Pigment*. Applicant: J.M. Huber Corporation. Inventors: Haverinen, J.P., Seuna, E.H., Fordsmand, H
20. US5312485. *Precipitated encapsulated paper pigments and methods*. Applicant: J.M. Huber Corporation. Inventors: Wason, S.K., Withiam, M.C