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Characterization and Application of Prepared White Sand\$TiO_2$Core Shell as New Economically Multifunctional Paper Coating Pigment

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Abstract: White Sand\$TiO_2$ core-shell multifunctional pigments have been synthesized successfully by simple chemical method. Economical white sand is used as a coating pigment for the first time in this work. The prepared pigments were investigated physicochemically by many techniques. Then they were applied in paper coating mixtures and their influence on coated paper properties were systematically investigated. SEM and EDAX investigations proved that the TiO_2 shell of the prepared pigments is thin and it was in the range of 30-50% of the whole core-shell structure. The application of the prepared pigments in coating mixture increased brightness, opacity, burst strength, burst index, tensile strength, tensile energy absorption, print density and smoothness of the coated papers. The magnificent effect has been obtained upon increasing the percent of TiO_2 shell in white sand\$TiO_2$ core-shell. Air permeance started to decrease then increased with increasing the percent of TiO_2 shell.

keywords: White sand, TiO_2, Paper coating, Multifunctional pigments, Core-shell

1.Introduction

The paper industry is continually searching for new thoughts to enhance paper products while competition and raw material prices are increasing, It is vital to produce high-quality paper at the most reduced expense and limit natural issues; numerous scientists have advanced an assortment of methodologies for this objective [1]. Coating applications can be done on paper or paperboard to include them more claim to fame or enhance their qualities [2].Generally, the quality and optical properties of the coated paper are enhanced by filled cavities, covered fibres and leveling paper surface. Moreover, one of the most critical functions of the paper coating is providing better printing properties in terms of print quality, image reproduction, printability and surface strength [3]. Paper mixture consists essentially of pigment, binder, additives and water. Pigment is the most abundant fragment in the coating mixture, so pigment is the most vital part controlling the properties of the coating materials [4]. Pigments are typically derived from various minerals, such as kaolin clay, calcium carbonate, silica and titanium dioxide pigment; these pigments may be used individually or mixed together [5-7]. Recently, great efforts have been improved to comprehend the effects of pigment mix on the paper coating properties [8]. TiO_2 has been utilized as an exceedingly qualified white pigment in paper coating for its points of interest such as high refractive index, superior brightness, high level of whiteness, ideal hiding power, antimicrobial action and insolubility in alkaline and acidic media [9-10]. These days, in view of titanium resources shortness and the high cost of TiO_2 pigment, discovering substitute materials to supplant TiO_2 has been of far-reaching significance [11]. TiO_2 has also been reported to have antibacterial growth inhibition characters; it enhances sunlight for killing bacteria in aqueous solution.

Core-shell theory presents a new easy route to obtain superior and eco-friendly cost saving pigments. The principle idea in core-shell preparation is precipitating thin shell layer of active or high cost material on a cheap core (waste, natural ore or extender) which represents the major component that comprises the new pigments in concentration about 80% of its composition. The combination of core and shell compounds prompted the creation of new pigments with enhanced properties not the same as its individual segments; consequently these enhanced properties can prompt the change in the effectiveness of coated paper containing these new pigments [12-14].

The aim of this work is to prepare a new multifunctional pigment based on bulk (core) of white sand with shell of titanium dioxide layer. White sand is a natural ore in the eastern desert of Egypt composed mainly of 98% silica. White sands have got the most diversified use among all the non-metallic minerals, because of its natural occurrence, unique physical properties such as hardness, heat and chemical resistance as well as economical price [15]. Three different pigments with different TiO_2 concentrations were prepared to relieve problems such as expensive cost as well as expanding the scope of application of cheap economic raw materials as white sand. These pigments were prepared using simple chemical economically feasible techniques, which enable them to supplant traditionally pigments with nearly similar effectiveness and sometimes can outperform their properties.

2. Experimental

2.1. Materials

The materials used in the present study to prepare white sand\TiO_2 core shell were: white sand (98.8779 % SiO_2, 0.8624 % Al_2O_3 and 0.0361 % Fe_2O_3) supplied from (Green Egypt Group for mining); its chemical composition is given in Table (1). Titanium tetrachloride and hydrochloric acid were supplied from (Sigma-Aldrich Company). For coating mixture preparation acrylic copolymer latex (Acronal S801, BASF) with 50% solid content and sodium hexametaphosphate dispersant (99%, Fine chemical company) were used.

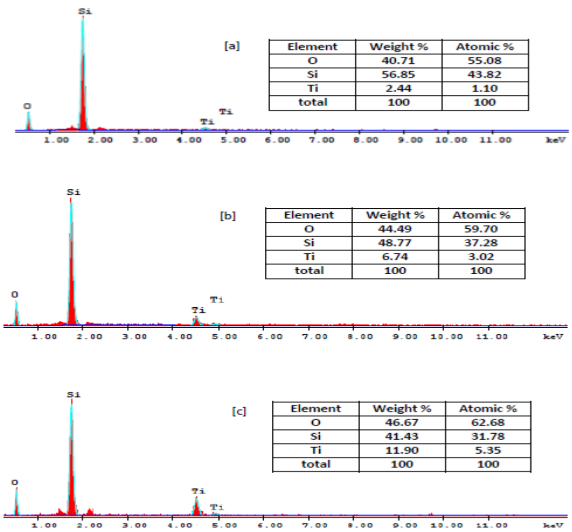


Fig.1 EDAX analysis of white sand\$TiO_2$core-shell pigments a (A), b (B) and c (C)

Table 1. Chemical and physical properties of white sand [16].

Chemical composition	Physical Properties				
	Specific Gravity	Moisture%	Hardness	pH	Brightness
98% SiO_2	2.60	0.15	7	9	86

3.1.2 XRF results

XRF results in Table 2 were found to be in high agreement with EDAX results which showing that SiO_2 is the major content of the prepared core shell pigments while the TiO_2 concentration increased in the order A<B<C in the prepared pigments.

Table.2 XRF analysis results of the White sand/TiO_2 prepared pigments

Main constituents (Wt %)	White sand\TiO_2 (A)	White sand\TiO_2 (B)	White sand\TiO_2 (C)
SiO_2	90.66	83.45	79.5
TiO_2	6.62	14.28	18.05
Al_2O_3	0.095	1.21	0.96
Fe_2O_3	0.08	0.09	0.08
Cr_2O_3	0	0	0
MgO	0.16	0.19	0.17
CaO	0.06	0.05	0.06
K_2O	0.01	0.01	0.01
Na_2O	00	0.04	0.04
P_2O_5	0.02	0.05	0.03
SO_3	0.02	0.03	0.03
Cl	0.23	0.05	0.10
LOI	2.065	0.785	0.97
Total	100	100	100

3.1.3. SEM analysis and the morphology of the prepared core-shell pigments

Fig. 2 shows the micrographs of the white sand and the prepared pigments with different TiO_2 concentrations using SEM. From the featured photos, it can be seen that, the white sand particles have an organized platelet structures Fig. 2a. In the case of core-shell pigments another phase appeared on the surface (Fig. 2 b, c and d) showing the presence of different structures, i.e. different component in the same compound, the more crowded surface has higher shell concentration. These two structures cannot be separated as they are welded to each other and this is confirmed by the TEM photos shown in Fig.3 The results show two particle shapes which are overlapping with each other and there is no separate structure of either of them appearing separately which confirms the formation of core-shell structured particles.

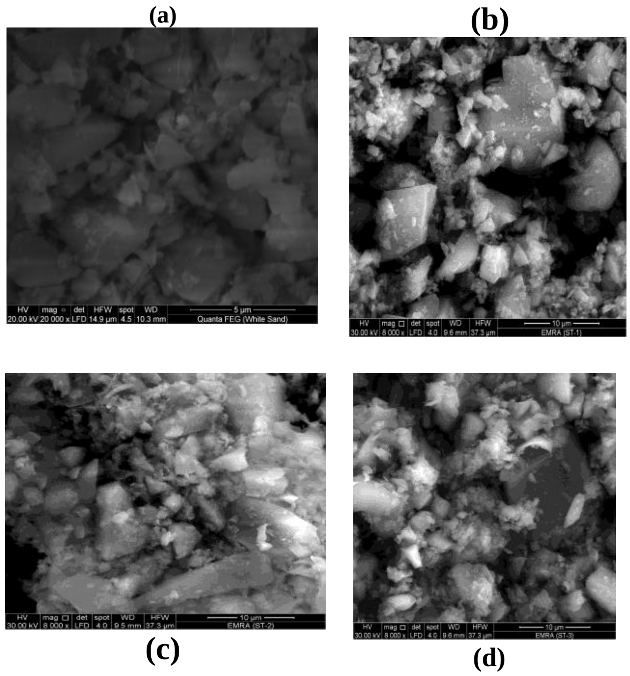


Fig. 2 SEM micrographs of white sand and white sand /TiO_2 (a) white sand (b) pigment A (c) pigment B (d) pigment C

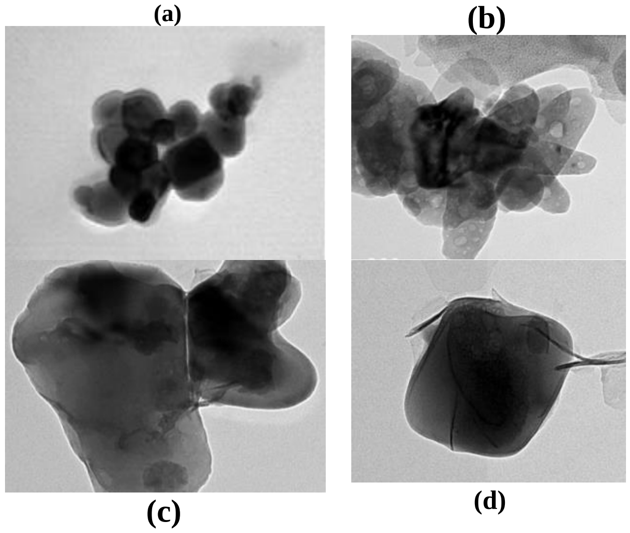


Fig.3 TEM micrographs of white sand and white sand \TiO_2 (a) white sand (b) pigment A (c) pigment B (d) pigment C

3.2. Application in Paper Coating

Optical properties

The paper surface optical properties are the most required parameters due to their aesthetic appearances; however, they play a vital role in printing or writing show through the paper product. The characteristics are determined by reflecting ability, absorbing capacity and penetration of light. **Brightness** measures the reflectance percentage of blue light by the paper and plays an important role in the paper's print contrast and image legibility. Fig.4a illustrates the effect of the prepared white sands\TiO_2 pigments on brightness of the prepared coated paper. The high refractive index of TiO_2 increased the coated paper brightness with a percentage of 4.3% upon increasing the shell of titanium dioxide in the prepared pigment.

Opacity is the ability of a sheet to hide print on an underlying sheet or on the opposite of the sheet itself which is potential demand in a packaging connection where the paper is applied as an overwrap on top of a printed surface [17]. Printing opacity is the ratio of the reflectance of a black solid printed area viewed through one thickness of paper under test to the reflectance of a pile of the non printed paper. For an entirely transparent paper, the opacity ratio is 0% while the ratio for a completely opaque paper is 100%. In order to keep the opacity of paper high, it is essential to increase the scattering coefficient as high as possible by encouraging the inter-reflection of light between fibers in paper [18]. The opacity of the coated paper slightly somewhat increased after increasing the content of titanium dioxide shell as showed in Fig.4b.

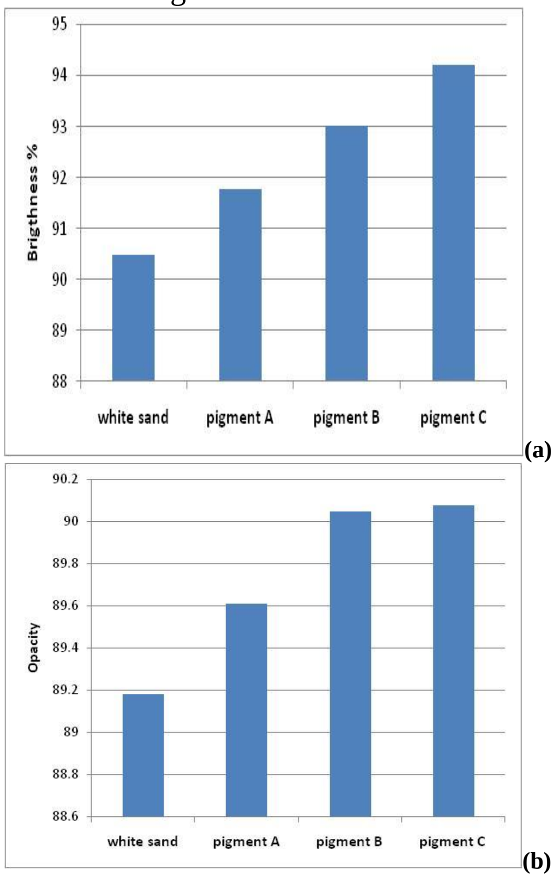


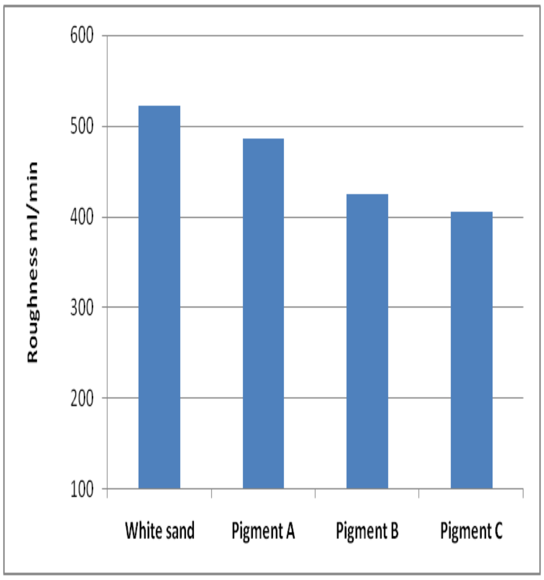
Fig. 4 (a) Brightness (b) opacity of white sand, white sand\TiO_2 prepared pigments A, B and C.

Physical properties

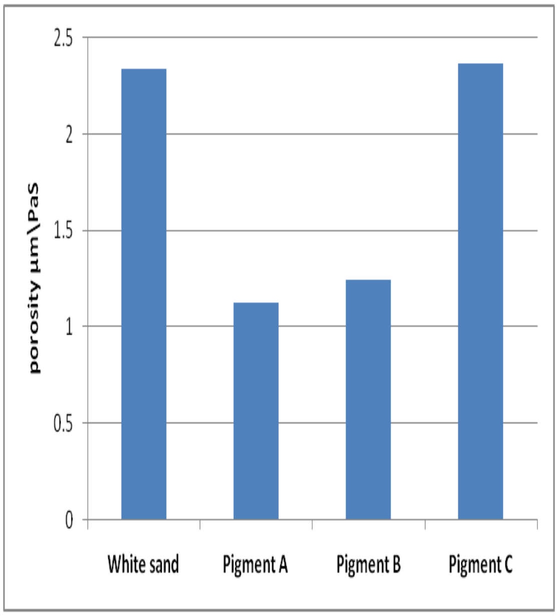
Uniformity of the paper physical properties continues to be one of the most serious quality items in paper industry. However because of the paper manufacturing process itself, defects cannot be eliminated completely from paper.

Paper roughness or smoothness is represented differently as the time for a fixed volume of air to leak out, moving between a paper surface and a metal plate clamping the sample. Paper smoothness is the evenness and flatness of the surface and plays a vital role in digital print image quality. Rougher surfaces contain higher peaks and valleys as compared to smoother surfaces. The lack of these surface irregularities permit toner particles to adhere to the surface more evenly producing a better image [18]. Fig. 5a shows that the increase of titanium dioxide content in the shell led to substantial decrease in coated paper roughness with a percentage of 22%. It's evident that white sand coated paper has the higher roughness value this might be attributed to the interparticle friction, less spherical and less convex of the white sand particle [19].

Fig. 5b shows the **permeability's (porosities)** of the coated paper samples for white sand and white sand/TiO_2 samples. It's evident that sample A has the lowest air permeance value. As the content of titanium shell increased the porosity of coated paper significantly decreased then increased until reached to the value of paper coated with white sand alone.



(a)



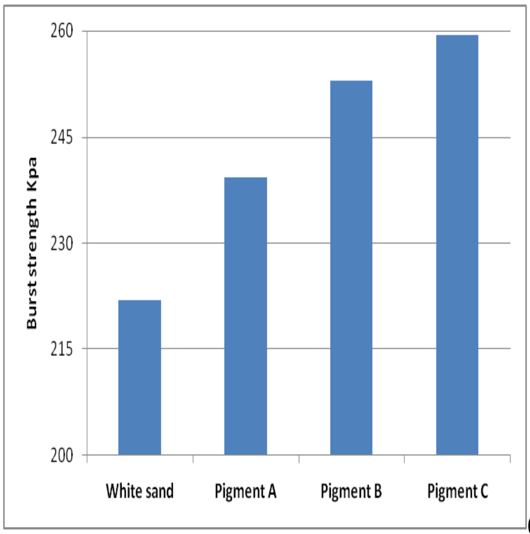
(b)

Fig. 5(a) Roughness (b) porosity of white sand, white sand/TiO_2 prepared pigments A, B and C.

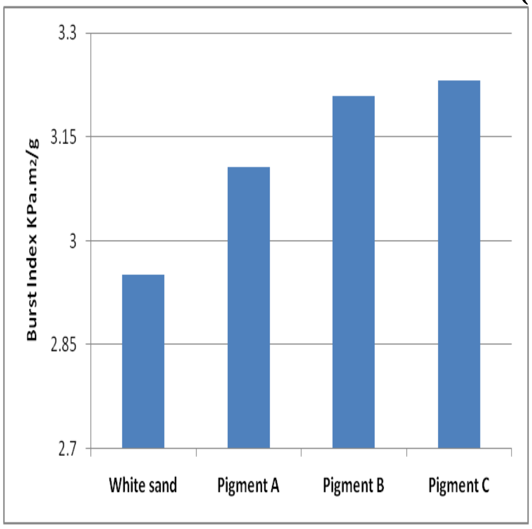
Mechanical properties

The paper coated mechanical properties are vital in the investigation of the bending and compressive deformation that coated paper faces in a printing machine, e.g., paper handling and runnability [20]. The mechanical properties of pigmented coating paper are delicate to changes in the pigment type and morphology, the binder properties, and the degree of the pigment coverage with the binder [12].

Bursting strength is one of the most broadly handled strength measurements tests for paper and paper board. The fundamental purpose of this test is to estimate the resistance of the paper to rupture in use. The bursting strength of paper or paperboard is a complex strength property, which is influenced by various other properties of the sheet, tensile strength, and stretching [21]. TiO_2 is hard and tough pigment (6- 6.5 Moh) which enable the pigment to withstand any applied force. Increasing the content of TiO_2 shell greatly enhanced the resistance properties and the hardness properties. Fig.6a and 6b shows the burst strength and burst index respectively of the coated papers for white sand and A, B, C prepared pigments. It's evident that burst strength increases with a percentage of 17% and the burst index increases with a percentage of 9.4 % by increasing the content of TiO_2in the shell in relation to white sand.



(a)



(b)

Fig. 6 (a) Burst strength (b) Burst Index of white sand, white sand/TiO_2 prepared pigments A, B and C.

Tensile strength is a magnitude of the force needed to break a paper strip with a standard length and width attached between two clamps under a standard rate of extension. It is represented as kilo-Newton per meter (kN/m). Tensile strength associates well with the durability and serviceability of several papers, such as a wrapping, bag, gummed tape, and others restricted to direct tensile stresses in converting or in use. In printing papers, tensile strength shows the potential resistance to breaking when the web is forced to tensile forces during traveling from the roll at the press mechanism in the web-fed printing system [17]. Fig. 7 shows the effect of the prepared white sand/TiO_2 pigments and white sand on the tensile strength of coated paper. Increasing the content of titanium dioxide shell in relation to white sand led to an increase in tensile strength with a percentage of 85% comparing with the sample containing white sand only.

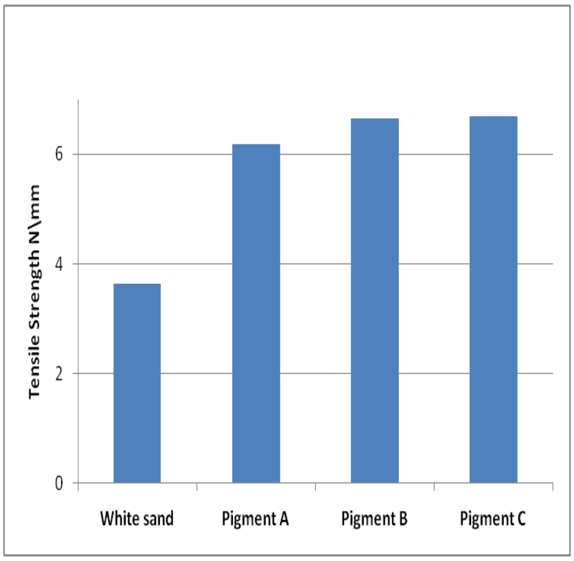


Fig.7 Tensile strength of white sand, white sand/TiO_2 prepared pigments A, B and C.

Tensile energy absorption (TEA) is a very significant paper strength measurement. It is the area below the stress-strain curve, after which the paper is stretched and ruptured. Its results are estimated as a measure of the paper toughness. TEA is very valuable in papers that are likely to be exposed to local stress such as grocery bags [17,20].The TEA showed a pronounced increase with increasing content of titanium dioxide shell in relation to white sand with a percentage of 72% comparing with the sample containing white sand only as shown in Fig. 8

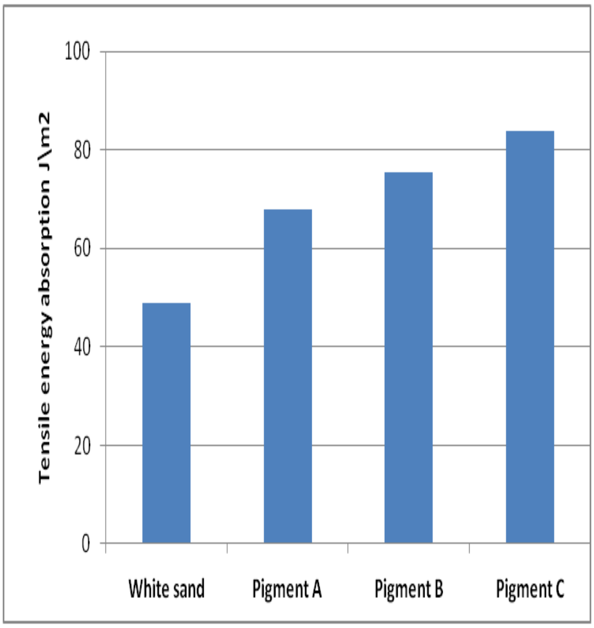


Fig.8 Tensile energy absorption of white sand, white sand/TiO_2 prepared pigments A, B and C.

Print quality of coated paper

The print density or the reflection density is a measure of contrast. In other word, it represents how well the paper surface is covered by ink after printing. As illustrated in Fig. 9 increasing content of titanium dioxide shell has a significant effect in increasing print density with 94% comparing with the reference coated paper containing white sand only.

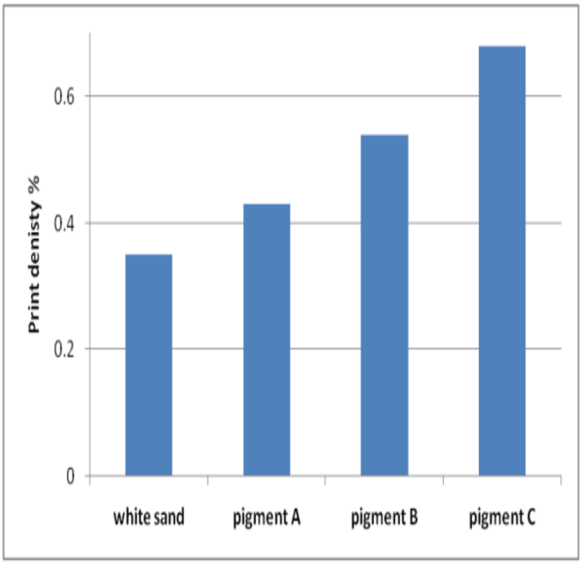


Fig.9 Print density of white sand, white sand/TiO_2 prepared pigments A, B and C.

4. Conclusion

In this work, a new approach for improving the paper coating optical, physical and mechanical properties using low-cost white sand pigment for the first time which is regularly a continuous requirement for paper making, was performed. The modification involved preparation of a multifunction white sand\TiO_2 core-shell pigment with three concentrations of titanium dioxide that forms the shell. The obtained results led to the following conclusions:

- Coated paper roughness was significantly decreased upon increasing concentration of titanium dioxide shell in white sand\ TiO_2 core shell pigments.
- Increasing in the concentration of titanium dioxide shell led to a significant increase in tensile strength, bursting strength, and burst index were also significantly improved.
- The print quality of the paper coated with the new white sand\ TiO_2pigment was also improved by increasing titanium dioxide shell concentration.

4. References

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