Asian Journal of Chemistry; Vol. 23, No. 8 (2011), 3747-3754

ASIAN JOURNAL OF CHEMISTRY

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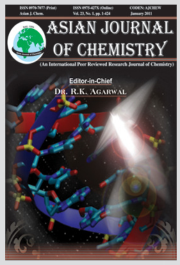

Nano-Hybrid Surface Coatings on Uncoated Papers from Softwood Fibers and Woodfree Fibers and Printability

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(*Received*: 7 February 2011; *Accepted*: 29 April 2011) AJC-9892

Nano-hybrid coatings are deposited as a top-coating onto various paper substrates from a stable dispersion with maximum solid content of 100 wt. %. The nano-hybrid coatings that blend of fluocarbon resin and polymers of highly branched dendrimers in a matrix of hydrocarbons was applied on various basis of papers from consisting of both softwood fibers and woodfree fibers. Scanning electron microscopy images showed complete nanoparticle coating on these papers. The morphology, physical characteristics and chemical surface properties of the coatings are discussed using scanning electron microscopy. The thickness of the nano-hybrid coating was estimated as 2-3 mm for woodfree papers corresponds to average 1 % nanoparticle loading of the fibers. The basis weight of coated paper handsheets from woodfree fibers showed that nanoparticle coating gave handsheet weight higher than the weightness of the first papers. The paper handsheets prepared with nanoparticle-coated fibers had higher water resistance. Due to the high printing properties (flexo printing test and off-set printing test) and water repellence (reduction of Cobb-values), the interaction of the nanoparticle coatings with the woodfree paper results in improvement of the mechanical paper strength and is attributed to hydrogen-bonding between the nanoparticles and the cellulosic fibers.

Key Words: Nano-hybrid top-coating, Uncoated papers, Water resistance, Printability, Colour differences.

INTRODUCTION

Recently, the word "hybrid" is seen very often. Some examples are the hybrid car, or hybrid version of a computer software, hybrid type mobile phone, *etc*. The dictionary meaning of the word "hybrid" is "a mongrel" or "a thing made by combining two different elements". If so, what is the meaning of "hybrid" in materials science? It is literally "something that is obtained by mixing different types of materials" and becomes a new material that can be called a "mongrel". Therefore, a hybrid of organic and inorganic is a combination of organic materials and inorganic materials. In particular, they may also be called polymer hybrids to emphasize that polymer constituents are involved. However, in order to distinguish them from the conventionally known composites that are mere mixtures, it is necessary to call the materials "hybrid materials" when the level of mixing of the different types of materials is at the nanometer level, or sometimes at the molecular level. A scale of the domain size is measured as 10^{-7}-10^{-8}. In such hybrid materials, it is possible to expect interesting characteristics that are not found in the organic polymer or the inorganic material independently. For example, they can have features such as being flexible like a plastic but have excellent mechanical strength and thermal stability[1-5]. Pulping, paper process chemistry, paper coating and recycling are key areas that can benefit from nanotechnology methods[6-12]. The creation of nano-hybrid layers is used essential for materials including porous and absorbent textiles, non-wovens, packaging paper or paperboard. The surface properties and water resistance of those substrates can be influenced by physical (drying, calendaring) and chemical (impregnation, coating) treatments. The styrene-butadiene latex is a successful emulsion-type coating for paper with superior film-forming properties, resistance to water and moisture and permitting rapid drying with low porosity[13-17]. Other water-soluble polymers such as polyvinyl alcohol (PVOH) are available as emulsions with a broad viscosity range and different degrees of hydrolysis, forming excellent impregnating agents[18] or barrier coatings[19] with good optical properties, ink-holdout, water resistance, hardness and durability (but often brittle) after drying. The latter properties depend on the degree of hydrolysis and eventual cross-linking with insolubilizers. Various polyester coatings were introduced as water-based systems[20]. The polyvinylidene chloride (PVDC) emulsion coatings provide aqueous systems with high solid contents, minimum viscosity and good barrier properties[21]. The other researches was focused during paper formation and drying, hydrogen bonding between cellulose fibers provides paper strength. To produce print quality paper, one needs to add silica, TiO_2, clay and other microparticles to adjust necessary brightness, opaqueness and wettability for paper. Controlled dispersion of these additives in paper is an important task and this microemulsion loading into paper is a well-known process. In addition to clay, silica and TiO_2, which are routinely added during the paper making process, $Mg(OH)_2$ or $Ca(OH)_2$ are added to paper for preservation and durability[22,23]. A silica nanocast on wood fibers has been demonstrated[24] and their lumen loading with $CaCO_3$ and Fe_2O_3 nanoparticles has been achieved[25-27]. Coating nanoparticles onto and/or into woodfree papers before paper formation has not been established. Some paper focuses on the physical properties of nanoparticle coated papers and illustrates the interactions between the nanoparticles and cellulose fibers. Once it is known that aqueous nanoparticle dispersions interact well with the paper substrate, it may further be tested in combination with various coating formulations. Similar results were demonstrated in the works by a Belgian group[28]. Multiple additives or pigments are commonly included for tuning barrier properties[29] or printing properties[30]. On the one hand, silica or calcium carbonate pigments optimize the ink-jet print quality[31]. On the other hand, mineral pigments such as (delaminated) talc[32], kaolin clay particles[33], or exfoliated nanoclays[34] improve the barrier resistance.

However, there is no report on organized surface top-coating of nanoparticles on cellulose fibers. The purpose of this work is to surface coating different basis weight of papers and checked on woodfree papers and softwood papers printability. In this work, we applied the nano-hybrid coatings that blend of fluocarbon resin and polymers of highly branched dendrimers in a matrix of hydrocarbons was applied on various basis of papers from consisting of both softwood fibers and woodfree fibers. We systematically analyzed these nanocoatings with scanning electron microscopy (SEM) images showed complete nanoparticle coating on these papers. Various basis of woodfree paper and softwood paper handsheets were measured for variations in weight in grams, thickness, cobb value, surface roughness, colour differences in offset printing, colour differences in flexo printing, remission curve of offset printing, dot area of flexo printing.

In this paper, we consider, nano-hybrid coating formulations have a complex composition and take up a considerable part of the paper weight. There is environmentally friendly and printable coatings that are compatible with woodfree paper coating processes and can be deposited with appropriate water resistance and high solid colour. The hybrid coatings should combine better woodfree papers than softwood papers, water repellence, surface roughness, optical properties and printability as an alternative to conventional waxed packaging paper. Woodfree papers that is coated nano-hybrid are known for good ink receptivity and they are mostly present specific hydrophobic action at the paper surface. It observed that which type papers give better results with nano-hybrid coating. At the same time how impact the printability values from nano-hybrid coating materials.

EXPERIMENTAL

The major part of the articles coated with nano-hybrid such as packaging papers from softwood and woodfree fibres actually have optimum protection against moisture (Table-1). The use of fluorocarbon-free water-repellent agents, that are on a level with a fluorocarbon resin finish as far as the water repellency is concerned. Achieve to this, the surface structure obtained with Rudolf Duraner A.S. products is homogenous over the whole top layer. Primary advantage is that Rudolf Duraner A.S. products are environmentally harmless. No durable decomposition products, APEO (alkylphenol ethoxylates) or solvents are used. The hybrid nanoparticles used is blend of fluorcarbon resin and polymers of highly branched dendrimers in a matrix of hydrocarbons. The nano-hybrid were purchased from Rudolf Duraner A.S. as "Product Hb-Sa-D-Hidrofobi materials"[35]. In the range of pH 8-9.

TABLE-1
TYPICAL PROPERTIES OF NANO-HYBRID COATING

Mechanical properties	
Specific name	Product Hb-Sa-D-Hidrofobi materials
Specific compound	Fluorcarbon resin polymers of highly branched dendrimers in a matrix of hydrocarbons
Storage temperature	5-30 ºC
Form	Pad shape
Color	White from beige
Smell	Characteristic
Thermal properties	
Melting point	Unspecified
Boiling point	100 ºC
Flare up point	> 65 ºC
Catch fire point	371 ºC
Heat of combustion	371 ºC
Heat of dissolutions	> 60 ºC
Threat of explosion	No
Steam pressure	20ºC'de: 23 hPa
pH volume	At 20 ºC': 8.0-9.0

Uncoated softwood papers and woodfree papers, cut in bundles of A3 sheets as commercial press-size, was supplied by International Paper Company, Alkim from Turkey. This nano hybrid coating material was used on whole papers surface, both softwood fibers and woodfree fibers. Handsheets with various basis weight were coated with nanoparticles. Uncoated papers was used as a control. Offset paper is a WFU paper with ISO brightness > 80 % and a basis weight of 40-300 g/m^2. Surface strength and low linting are the main parameters, but also brightness and opacity are important[38]. Six grades of paper were obtained from Alkim (Izmir, The Turkey) and used as names: (i) WP-70 has basis weight Bw = 70 g/m^2, (ii) WP-80 has basis weight Bw = 80 g/m^2, (iii) WP-90 has basis weight Bw = 90 g/m^2, (iv) WFP-70 has basis weight BWF = 70 g/m^2, (v) WFP-80 has basis weight BWF = 80 g/m^2 and (vi) WFP-100 has basis weight BWF = 100 g/m^2.

The paper substrates were made from bleached long fiber pulp and short fiber sulphate pulp and contain additional optical brightening agents. The woodfree paper substrates consist of chemical pulp. Just before the handsheet printing, the coated wood papers and woodfree papers were tested in basis weight, thickness, cobb, surface roughness. A3 dimensions and various weight handsheet samples were used with uncoated wood paper and woodfree paper as listed in Tables-2.

Methods

Nanocoating procedure and method: Two hundred and fifty milliliters hybrid nanoparticles was used. All the concentrations were mixed for 10 min before use. The concentration of hybrid was used 100 %. Nanoparticles were alternately adsorbed onto the surface of papers. Five-times coating was conducted for each type of papers. Each sheet coating with MDF/749 Zimmer using a silk gaze consisting of 100 frequency. After the coating process, samples was layed for drying time of approximately 3 h in room temperature. Each sheet fixed different temperature level. First, top-coating was not fixed temperature. The coating was absorbed with valuable water level. Second nano-hybrid coated papers fixed various temperature level and the temperature progressively raised to a maximum of 160 ºC. While further heating at130-160 ºC, a sudden stop in water-resistance was characteristic for the initiation of nanoparticle formation.

Printing procedure and method: The wood free papers (WFP) and wood papers (WP) were subsequently conditioned for at least 24 h at 23 ºC and 50 % RH (relative humidity) before printing and subsequent measurements were made. Two printing technics were used according to TAPPI T494-014-88 standard using C1 offset IGT and F1 flexo IGT. The printability and ink-compatibility of the uncoated papers was first evaluated by offset printing, using C1 off-set IGT printing process and a commercially available pigment-based orange ink supplied from DYO printing ink industry and trade SA that is one of the first printing ink manufacturers in Turkey. Off-set IGT printing force was evaluated 650 N. The ink is commercially named Dyo Quick fresh, AS 256 Orange. Its' other properties is light fastness 5-6, alcohol+, alkaline+, nitro+. After printing, the ink was allowed to dry for about 1 day in air and the printed samples was measured for solid density.

A second printing test was done using a commercial flexo printing process with original Black printing inks (Dyo Trade SA, Turkey). Flexo IGT printing force was evaluated 250 N. and anilox force was set up 150 N. After printing, the image was allowed to dry for about 1 day and the printing pattern was analyzed for a black coloured image where solid density. The printing quality on uncoated and woodfree uncoated papers was evaluated from sharpness of the printed image. Colour differences (DE), remission curve was calculated using the TECHON spectrophotometers at each printings techniques. Handsheets were measured according to Technical Association for Pulp and Paper Industry TAPPI standard.

Morphological characterization of paper: The coating morphology was investigated by scanning electron microscopy. Scanning electron microscopy was performed with SEM (JEOL, JSM 5410 LV) equipped with backscattered and secondary electron detectors coupled with EDS was employed to observe the morphology of the uncoated and coated samples. The SEM-EDS provides detailed imaging information about the morphology and surface texture of individual particles, as well as elemental composition of samples. The three most common modes of operation in SEM analysis are backscattered electron imaging (BSE), secondary electron imaging (SEI) and EDS. In this study, BSE and EDS were used to characterize the samples. BSE provides visual information based on gray-scale intensity between chemical phases. Backscattered electrons are high-energy electrons that are reflected directly from the specimen surface.

Measurement methods of the physical properties of paper: The surface roughness (pps) parameters Ra (average roughness), were calculated on a 297 mm × 420 mm standard A3 size and averaged from three measurements using with TECHNIDYNE /profile plus (pps). The surface roughness was measured both front and back side.

The basis weight (g/m^2) was measured with a Etscale. An average of three measurements was made with a rounded samples. The materials before and after coating used in the experiments were first conditioned at laboratory and cut in pieces of 100 cm^2 using a cutting apparatus and their mean weight was determined in accordance with ISO 3801 upon conducting three measurements.

The thickness of papers were evaluated with LW Micrometer 51 testing machine. An average of three measurements was made. This simple thickness tester measures the thickness of paper, cardboard, plastic films, *etc*. This tester is without motor, mesuring range 0-10 mm., scale value 0.001 mm, inside depth (overhang) 160 mm, pressure foot size of diameter 10 ± 0.05 mm, measuring pressure 2 ± 0.01 kPa, lowering speed 2.5 mm/s. Test surfaces from each handsheet were used according to ISO 534, 3034, EN 20534, SCAN P7, P31, DIN 53105, 53353 standard and the thickness value was calculated using the above ISO standard. The thickness was measured by the time needed for three times measuring and also given averaging.

TABLE-2
PHYSICAL CHARACTERIZATION OF PAPER HANDSHEETS BEFORE COATING PROCESS

Sample name	Basis weight (g/m^2)	Thickness (mm)	Surface roughness (front) (pps)	Surface roughness (back) (pps)	Cobb (back)
Wood papers					
WP-70	69.0	0.860	6.96	6.96	22.2
WP-80	81.0	0.104	8.42	8.42	22.0
WP-90	89.4	0.106	6.26	6.26	20.8
Wood free papers					
WFP-70	69.7	0.085	7.20	7.20	25.9
WFP-80	80.5	0.990	7.43	7.43	23.6
WFP-100	102.0	0.115	6.53	6.53	27.9

WP = Wood papers; WFP = Wood free papers.

The water absorptiveness of the substrates was determined according to the Cobb-test method. Samples were cut to 14 cm × 14 cm and clamped inside a ring of diameter 10 cm. A 100 mL sample of water was poured into the ring and remained in contact with the paper for 60 s. The wet sample was afterwards dried in between two pieces of blotting paper. The water absorptivity A = (W2 -W1)/100 (g/m^2) was calculated from the sample weight W1 before and W2 after test. The cobb tester is a simple instrument which measures the water absorptiveness of paper, cardboard and corrugated fiberboard under standard conditions. Test method was set up as test area (standard) was 112.8 diameter, water depth was 10 mm, water volume was 100 mL. Test surfaces from each handsheet were used according to ISO 535, DIN-EN 20535, TAPPI T-441 standard using a Rycobel Group Cobb Tester (Model D-11-13-cobb) and the cobb value was calculated using the above TAPPI standard. The water absorptiveness of paper was measured averagely three times.

Measurement methods of the printed samples: Colour measurements of the coated samples were conducted in accordance with the CIELab system using TECHKON SpectroDens reflectance spectrophotometry and Spectra Connect additional software modules. Colorimetric measurements can only be compared when the measurement conditions are the same in printing industry: polfilter: off, white reference: Absolute, illuminant: D50, observer: 2º. When selecting "Auto" in the polarizing fitler setting, there will be automatically the polarizing filter inactivated when making colorimetric measurements. For the purpose of the measurements, an 2º observer and a D50 light source were also used.

The colour distance ΔE* is displayed with two digits. Additionally the components ΔL, Δa and Δb can be seen. But in printing industry is accepted ΔE < 3. The measurement function ISO-check enables the fast check of a print with regard to the compliance with the ISO standard values ISO 12647-2. The Lab-values, ΔE-colour differences and the spread of the printing inks orange and black are documented.

RESULTS AND DISCUSSION

Physical properties: The paper handsheets for coating application were first measured as thickness, basis weight, surface roughness and cobb values (Table-2).

After handsheets was made from equal amounts of coating materials, first values compared resulted paper which was coated nano-hybrid. The handsheets result details were shown as follows. The details consist of basis weight, thickness, surface roughness (both front and back side), Cobb values (both front and back side). The surface roughness test results are shown in Figs. 1 and 2 and Table-3.

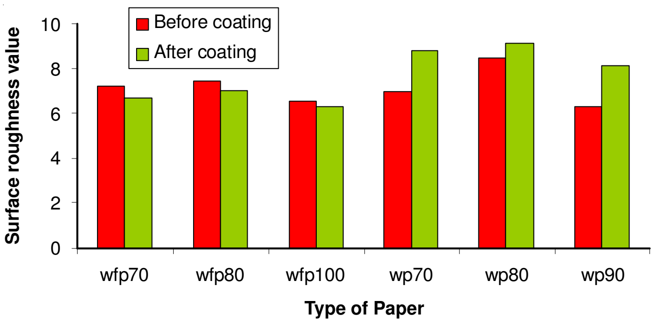


Fig. 1. Roughness test (front side) results for handsheets made from nano-hybrid coating. The first set of handsheets was prepared as described in Table-1

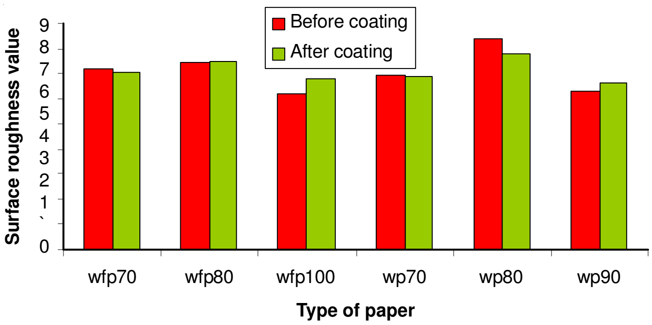


Fig. 2. Roughness test (back side) results for handsheets made from nano-hybrid coating. The first set of handsheets was prepared as described in Table-1

Wood papers that made from bleached long fiber pulp and short fiber sulphate pulp and contain additional optical brightening agents, coated with nano-hybrid gave the highest roughness of 130 %. Therefore, the roughness increase is about 121 %. The wood paper substrates roughness increase is about 20 %. The woodfree paper substrates which consist of chemical pulp roughness decrease is about 6 %. There is no big difference in roughness between handsheets prepared from woodfree fibers coated with nanoparticles. The basis weight results were shown in Fig. 3.

All the paper handsheets with nano-hybrid coating gave almost the same weight value percentage. But the value percentage decreases with the increasing the basis weight. The

TABLE-3
PHYSICAL CHARACTERIZATION OF PAPER HANDSHEETS AFTER COATING PROCESS

Sample name	Basis weight (g/m^2)	Thickness (mm)	Surface roughness (front) (pps)	Surface roughness (back) (pps)	Cobb (front)	Cobb (back)
Wood papers						
WP-70	72.0	0.099	8.81	6.87	22.7	67.5
WP-80	84.0	0.114	9.10	7.82	76.6	80.3
WP-90	91.5	0.122	8.14	6.63	44.0	96.6
Wood free papers						
WFP-70	72.0	0.092	6.70	7.09	16.0	70.8
WFP-80	83.0	0.105	7.04	7.46	13.4	69.0
WFP-100	103.5	0.125	6.27	6.85	23.8	96.7

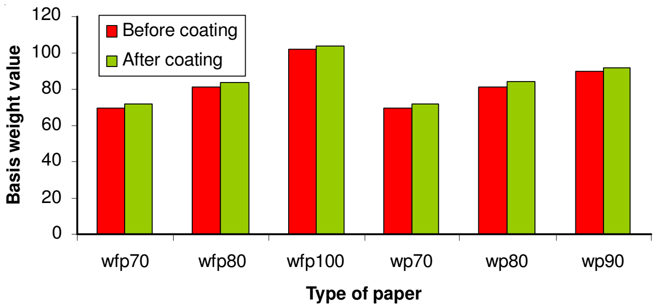


Fig. 3. Basis weight test results for handsheets made from nano-hybrid coating. The first set of handsheets was prepared as described in Table-1

wood paper substrates weightness increase is about 3 %. The wood free paper substrates which consist of chemical pulp weightness increase is *ca.* 2 %. There is no big difference in weightness between handsheets prepared from woodfree fibers coated with nanoparticles and wood fibers coated with nanoparticles. The thickness of papers results were shown in Fig. 4.

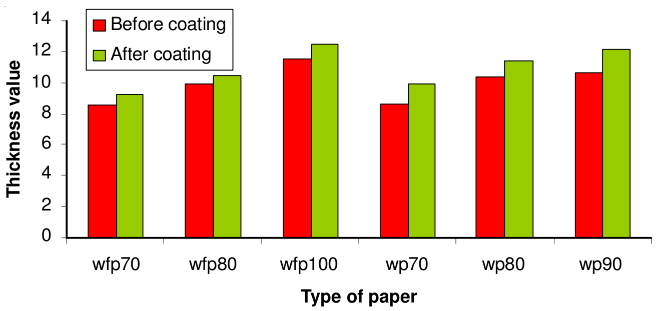


Fig. 4. Thickness test results for handsheets made from nano-hybrid coating. The first set of handsheets was prepared as described in Table-1

In all the papers, the sheet thickness increased: for wood free paper which consist of chemical pulp coating on 7 % and for wood paper that made from bleached long fiber pulp and short fiber sulphate pulp and contain additional optical brightening agents coating on 13 %. The nano-hybrid coatings increased thickness of the tested handsheets, but it drastically increased the wood paper. The handsheets with wood paper coatings had 15 % maximum thickness increase in this case.

The water absorptiveness of the substrates was demonstrated below. The front side results were shown in Fig. 5. Also, the back side results were shown in Fig. 6.

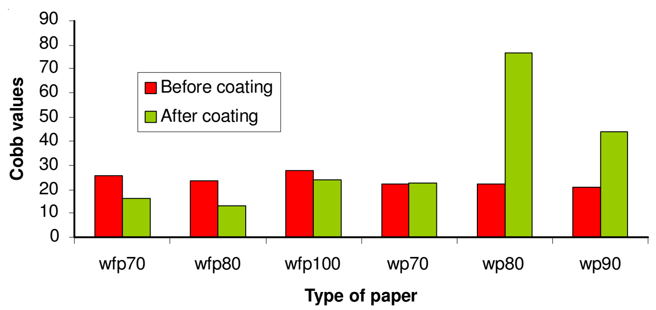


Fig. 5. Cobb-value test results for front side each handsheets made from nano-hybrid coating. The first set of handsheets was prepared as described in Table-1

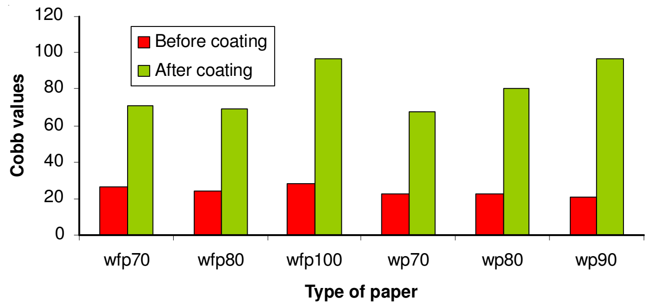


Fig. 6. Cobb-value test results for back side each handsheets made from nano-hybrid coating. The first set of handsheets was prepared as described in Table-1

The water repellence is characterized by absorption measurements according to the Cobb-test method, with lower Cobb-values representing lower water uptake. The values of uncoated papers made from woodfree are significantly lower than uncoated papers made from wood.

Experimental scatter may be relatively large and one reason may be attributed to the combination in coating. The coating material include fluorocarbon resin. The water repellence depends on the wettability of the paper surface as the hydrophobicity determines a first barrier against water uptake. The water penetration and absorption into the paper also largely depends on the homogeneity and internal structure of the coating. The back side results were shown in Fig. 6. The water penetration and absorption into the paper also drastically increased. That means nano-hybrid coating fend-off humidity and hold on.

Although the present coatings was a small amount of water. The improved water repellence achieved the fixing temperature was incresed at 130-160 ºC. The coating formulation was just optimized for set fixing temperature 130 ºC at least. The fixing time, fixing temparature results were shown with standard spray testing method in Table-4. According to standard spray test ratings, min 130 ºC and 1 minute fixing time enough to no sticking or wetting of upper surface[36].

TABLE-4
WATER REPELLENT OF PAPER HANDSHEETS AFTER FIXING

Sample name	130 (ºC)	140 (ºC)	150 (ºC)	160 (ºC)	Fixing time (min)
Wood papers					
WP-70	5	5	5	5	1
WP-80	5	5	5	5	1
WP-90	5	5	5	5	1
Wood free papers					
WFP-70	5	5	5	5	1
WFP-80	5	5	5	5	1
WFP-100	5	5	5	5	1

Printing results: The printing results were shown the CIE L*a*b* colour space that is the most popular colour system in the printing industry. Every colour is precisely described by three values: The L*-value stands for the luminance and can have values between 0 (a theoretical, absolute black) and 100 (a theoretical, ideal white). The a*-value describes the colour value on the green/red-axis (-a*: green, + a*: red) and the b*-value the colour value on the blue/yellow-axis (- b*: blue, + b*: yellow).

Tables 5 and 6 shows the standards accepted within the scope of the measurements as well as the ΔL, Δa, Δb and ΔE values of wood paper and wood free paper. The ΔE values of the samples represent the standard colour difference. If ΔE < 1, the difference between the two colour is little and if ΔE* > 1, the difference is substantial. The colour distance ΔE* describes how close two colours match. A value of 0 means that they are identical. DE-colour differences in the range of 5 can be seen by the human eye when reference and sample are close together and observed at the same time. The printability of coated wood papers and coated woodfree papers is evaluated by off-set printing the orange patch with a standard C10ff-set printer (Fig. 9). For coated wood papers, the printed area have diffuse borders due to the spread of ink in between the paper fibers. The large amount of ink adhering onto the tape applied to printed uncoated paper shows poor ink adhesion to the substrate. For coated woodfree papers, the borders of the printed area are better defined and lateral spreading of the ink is limited as the individual microdomains of the coating are covered with ink rather than the cellulose fibers. This results in good sharpness and gloss of the printed characters on the wood free paper nanoparticle coated surfaces compared to the wood paper nanoparticle coated ones (Table-5).

TABLE-5
COLOR DIFFERENCES FOR OFF-SET PRINTING OF PAPER HANDSHEETS

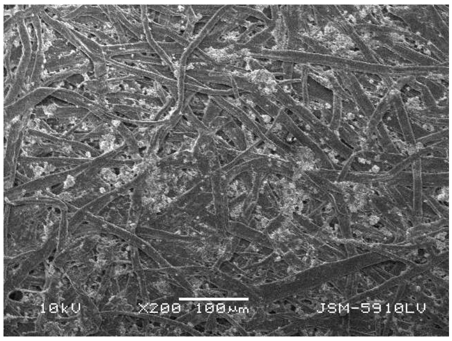
Sample name/off-set	ΔL	Δa	Δb	ΔE
Wood papers				
WP-70	1.53	-3.39	-16.78	17.19
WP-80	1.15	-2.50	-14.29	14.55
WP-90	-1.49	-2.53	-10.34	10.75
Wood free papers				
WFP-70	0.36	0.03	0.12	0.38
WFP-80	1.20	-1.29	0.11	1.76
WFP-100	3.00	-6.76	-5.49	3.06

TABLE-6
COLOR DIFFERENCES FOR FLEXO PRINTING OF PAPER HANDSHEETS

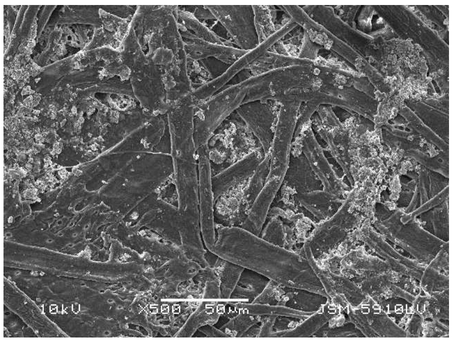
Sample name/flexo	ΔL	Δa	Δb	ΔE
Wood papers				
WP-70	19.37	0.35	-1.34	19.42
WP-80	17.97	0.41	0.01	17.97
WP-90	18.47	0.10	-1.56	18.54
Wood free papers				
WFP-70	2.49	0.42	1.50	2.94
WFP-80	3.06	0.31	1.07	3.25
WFP-100	2.96	0.28	1.24	3.22

The smaller amount of ink adhering onto tape applied to coated paper is indicative for good ink adhesion and fast drying times onto coated substrates, which is in fill due to the large pores in the coating structure. This formation of a coated morphology onto macroporous paper substrates favourably changes the capillary forces at the surface and therefore offers good printing properties. The coated surface serve as drainage channels for the evacuation of ink solvents, resulting in fast drying times. The microdomains serve as plateaus for the deposition and good adhesion of ink pigments. The printability of wood paper and wood free paper coated papers is also evaluated by off-set printing a orange colour image. But printability of wood free paper much more better and acceptable for industry standarts.

SEM observation of papers: The nanoscale morphology of uncoated papers from mechanical pulp and uncoated papers from chemical pulp was investigated with scanning electron microscopy. From scanning electron microscopy (Fig. 7), aggregation of nanoparticles into fibers with microdomains of 50-10 mm is observed. A detailed SEM picture shows that the nano-hybrid coating nearly penetrates into the paper web and wraps around the fibers. The relatively WFP- nanocoating (Table-3) provides good surface roughness and cobb-value. The coating surface contains spherical nanoscale structures with a mean diameter of around 200-250 nm. The smaller nanoparticle shapes observed in SEM images show particles that are both deeper penetrated into the coating and presented at the surface. The fundamental interaction between nanoparticles and the paper substrate will obviously happen at this nanofibrilar level. For coated papers, the nanoparticles are effectively located on top paper surface. Therefore the nanocoating application dramatically reduces the roughness parameters and cobb-values compared to uncoated papers.



(a)



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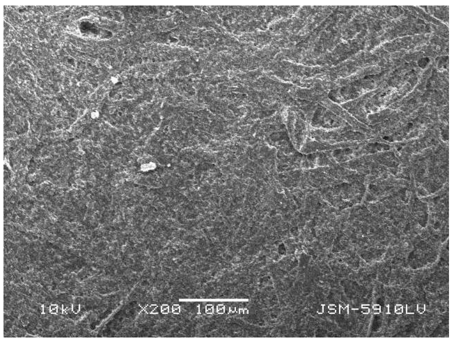

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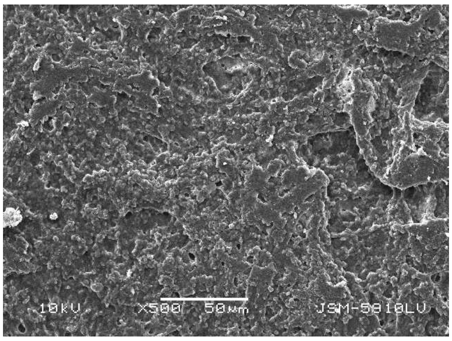
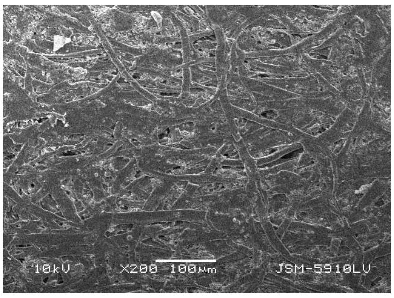


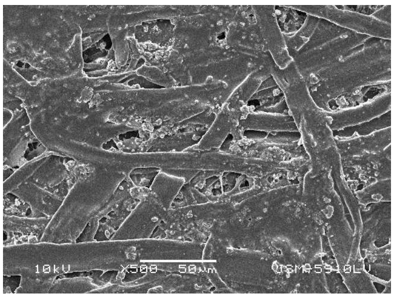
(d)

Fig. 7. Conventional scanning electron microscopy of WFP paper before and after coatings at different magnification: (a) 200× uncoated WFP, (b) 500× uncoated WFP, (c) 200× coated WFP, (d) 500× coated WFP

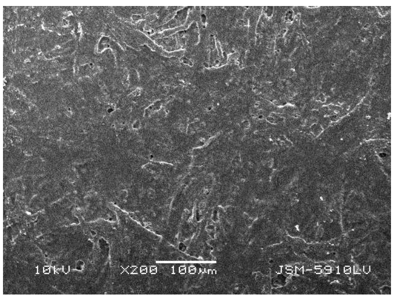
From scanning electron microscopy (Fig. 8), aggregation of nanoparticles into fibers and ink is observed. A detailed SEM picture shows that the ink and nano-hybrid coating absolutely cover onto the paper. The relatively WFP-nanocoating (Tables 5 and 6) provides good ink transfer on to surface. The best interaction between nanoparticles and the ink will obviously happen at WFP papers from consist of chemical pulp. Therefore the nanocoating application dramatically reduces the colour differences value compared to WP papers from consist of mechanical pulp.



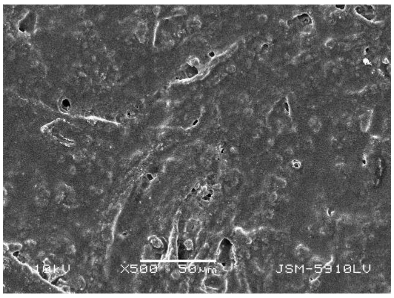
(a)



(b)



(c)



(d)

Fig. 8. Conventional scanning electron microscopy of WFP paper before and after ofset printing at different magnification: (a) 200× off-set printing on uncoated WFP, (b) 500× off-set printing on uncoated WFP, (c) 200× off-set printing on coated WFP, (d) 500× off-set printing on coated WFP

Conclusion

The major part of the nano-hybrid concentration mixed with fluorocarbon resins such as sportswear or outdoor articles actually do not need an oil-repellent finish but optimum protection against moisture. It was the development of fluorocarbon-free water-repellent agents, that are on a level with a fluorocarbon resin finish as far as the water repellency is concerned. Fluorocarbons resin have a hydrophobic properties that gives a chemical resistance to water (Fig. 9)[37].

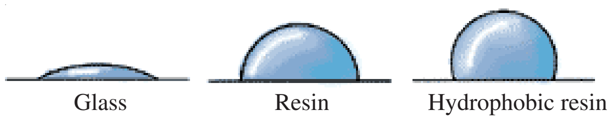


Fig. 9. Shape of water drops on the surfaces of fluorocarbon resins

Because uncoated papers does not have any coating materials on top. Wood free uncoated paper (WFU) or uncoated fine papers are containing mainly chemical pulps and 5-25 % fillers. The other papers made with using mechanical pulp. Wood free uncoated papers are of high quality and have a natural look and feel. The properties are good strength, high brightness and good archival characteristics. They provide a non-glare surface suitable for reading and writing[38].

By hybridization, it is noted that the resistance to papers increases compared to non-topcoating papers itself. flexo baski için. Such materials can be expected to be superior as barriers against water absorption. It is very interesting if the barrier characteristics to water is improved, because it is possible to use packaging and wrapping at the same time. Ambalajlamada oksijeni kesme. Nano-coating on top surface was applied to deposit organized spherical nanoparticles on wood paper and woodfree papers. Particularly cobb-test and SEM images showed that complete continuous nanoparticle coatings were achived on papers.

The thickness of the coating was estimated as 110 and 115 mm for WFP and WP and, respectively, which corresponds to coating 10 wt. % nanoparticle loading on the papers. The thickness test of paper handsheets prepared from nanocoated WFP papers showed that nanoparticle coating gave handsheet thickness of 7 % at 107 mm, which was 7 % lower than the thickness of the estimated from uncoated papers.

The coated substrates present higher water absorbance, better hydrophobicity and better water repellency than the uncoated substrates. The best results observed WFP papers. The imide content of the coatings can be determined from Cobb-test and spray test, which also indicates that the interactions between the nanoparticles and the cellulose substrates are located at the hydroxylic moieties, implying good adhesion of the organic nanoparticles to the substrate by means of hydrogen-bonding. The latter is also expressed in better colour differences of the WFP coated papers.

The better printability of nanoparticle coated surfaces compared to uncoated papers is illustrated by WFP papers after flexo printing and off-set printing, showing quick drying times and good ink adhesion. Moreover, the higher surface hydrophobicity offers higher density of deposited ink pigments by off-set printing. While favourable interactions of various paper surfaces with the nanoparticle coatings were discussed in this paper, it is believed that the presented nanoparticles have potential to be further employed in combination with organic or inorganic components to further tune the surface properties of paper and textile products.

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