



Calcium sulphate as pigment for improved functional properties of coated paper



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ABSTRACT

In the last few years, interest and demand of high bright paper have forced paper manufacturers to think new ways to improve brightness and whiteness of coated paper. Pigment coating is widely used to enhance the optical properties such as brightness, whiteness, and gloss of paper and paperboard. These optical properties are the most important for end user and also determine the final cost of coated paper. Calcium sulphate has inherent better optical properties compared to other conventional pigments for example ground calcium carbonate, precipitated calcium carbonate and kaolin clay. The present study was carried out with an aim to synthesize calcium sulphate using waste procured from phosphoric acid industry and to study its impact on the rheology of coating color as well as optical properties of coated paper. Addition of calcium sulphate improved the water retention property of coating color which can be helpful for improving the machine runnability. The results also revealed that calcium sulphate can be used as a pigment to produce coated paper of high brightness and whiteness. The brightness and whiteness of the coated paper were improved 4 and 15 points, respectively by using 50 parts of calcium sulphate as a pigment replacing clay from the coating formulation. The surface strength in terms of IGT pick value of coated sheets was found significantly comparable using calcium sulphate as pigment. The print gloss results were observed analogous with matt grade coated paper.

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1. Introduction

The principal need for coating is to improve certain properties of paper to make the printed image sharp, clear and more appealing to the eye [1,2]. The same carried out by filling the non-uniform surface of paper by applying pigmented coating and supercalendering to get desired properties of coated paper.

Pigments represent the major part of any coating color which constitute about 80–85% by weight. Pigment characteristics, such as particle size, size distribution, and morphology, play fundamental role in determining the coated paper quality like brightness, whiteness, gloss, print gloss etc. Different type of pigments e.g. ground calcium carbonate (GCC), precipitated calcium carbonate (PCC) and clay are used for paper coating [3]. GCC and clay are the most widely used pigments in paper industry and exploited in a large range of coating applications [4–6]. The major part of the calcium carbonate is GCC processed from chalk, limestone and marble. Calcium carbonates have high brightness, whiteness and oil absorption, but they form matt coatings. In addition, calcium carbonate

coatings produce good printability and require low binder demand in water-based coatings. Fine clay is used for better gloss, opacity and printability of coated paper because of its smaller particle size and platy shape i.e. a layered structure [6].

In the last few years, demand of high bright paper has forced paper manufacturers to think new ways to improve brightness/whiteness of paper [5]. Production of high bright bleached pulp, addition of high bright fillers and optical brightening agent (OBA) in the paper are selectively utilized to increase the brightness and whiteness of paper [7,8] while the coated paper with high brightness/whiteness level can be produced by using high bright pigments like GCC/PCC, addition of OBA/OBA carrier and reducing the load of supercalendering. But by reducing the supercalendering load, brightness and whiteness increased but the desired gloss could not be achieved.

Calcium sulphate (CS) has inherent better optical properties compared to other conventional pigments like GCC, PCC and kaolin clay. So it can be used to improve brightness/whiteness of paper. Calcium sulphate abundantly exists in nature in three different forms according to the degree of hydration: gypsum (calcium sulphate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), bassanite (calcium sulphate hemihydrate, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) and anhydrite (CaSO_4). Calcium sulphate also find its application in different industries as food

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additive, timbering, medical material, inorganic filler or intensifier in composite [9].

Phosphoric acid is produced either by acidulation of phosphate rock by a mineral acid (sulfuric or hydrochloric acid) in a wet process or by burning of phosphorus produced through electro-thermal process. Hydrochloric acid method generates large quantities of waste slurry containing calcium chloride and create environmental problem on discharge. For manufacturing 1 ton of technical grade phosphoric acid, generally about 1.2 ton of waste calcium chloride is generated [10].

This reported work is the extended work carried out earlier as mentioned elsewhere [11]. The current research work deals with the synthesis of calcium sulphate from effluent rich in calcium chloride collected from a phosphoric acid industry with an aim to develop different grades like matt or high gloss coated paper using calcium sulphate as pigment through single application of coating color. The synthesized CS was characterized by using various techniques like chemical analysis, X-ray diffraction, and scanning electron microscopy. The synthesized CS was also analyzed for its optical properties, particle size distribution, use in coating color formulation, effect on coating color properties and finally effect on coated paper quality.

2. Experimental

2.1. Materials

Coating base paper of 60 g/m² basis weight, having hardwood and softwood pulp combination, was used for coating application. Commercially available GCC (white powder, brightness ISO: 89.3%, 75% particle $\leq 2 \mu\text{m}$), coating clay (brightness ISO: 82.1%, 48% particle $\leq 2 \mu\text{m}$), synthesized CS as pigments along with styrene butadiene based synthetic binder (solid: 50%, T_g : 17 °C) and polyacrylate based dispersing agent (solid: 42%, nature: anionic) were used in coating formulation. Starch (brightness ISO: 85%) and polymeric acrylic copolymer (solid: 25%, nature: anionic) were used as a natural and synthetic rheology modifier, respectively. Chemical containing six-sulphonic group of triazinyl stilbene moiety and ammonium zirconium carbonate (AZC) based compounds were used as OBA (solid: 20%, nature: anionic) and insolubilizer (solid: 25%, nature: anionic), respectively. Calcium stearate based compound was used as lubricant (solids: 50%). These different chemicals were added to the color to have desired impact on coating rheology and final coated paper properties.

2.2. Synthesis of CS

Industrial waste rich in calcium chloride was procured from an Indian chemical company producing technical grade phosphoric acid. The CS was synthesized at ambient temperature under optimized conditions without addition of any rheology modifier and surfactant as reported in our previous work [11]. The synthesized CS was characterized for its optical and other properties as given in Table 1 [12].

2.3. Characterization of CS

Optical properties were measured by brightness tester (Elrepho, L&W). Horiba Laser Scattering Particle Size Analyzer (LA-950V2) was used to determine the median particle size and particle size distribution of all the pigments. The crystalline phases of the CS products were investigated by wide-angle X-ray diffraction (PANanalytical X'Pert PRO). The wavelength of the monochromatic X-ray beam was 1.54 Å and the range of the 2θ scan was 8–80°. The diffraction peaks of CS phases were compared to standard pattern (JCPDS, Card No. 041-0225).

Table 1
Characteristics of different pigments used in coating color formulation.

Properties	CS	GCC	Clay
Brightness, % ISO	98.1	89.3	82.1
CIE whiteness	97.8	85.1	72.2
Yellowness, %	0.24	2.62	6.51
L^*	99.3	96.6	94.7
a^*	0.03	0.16	0.36
b^*	0.11	1.30	3.23
Median particle size (D50), μm	0.21	0.94	1.71
% Particles $\leq 2 \mu\text{m}$	92	75	48
Span, $\{(D90-D10)/D50\}$	2.5	3.4	6.5

Surface morphology of product was characterized by scanning electron microscopy (SEM, JEOL JSM 6510 LV) after coating with an approximately 50 Å thick gold layer.

2.4. Preparation of coating color

Procedure for making coating color was followed as given in reported work [11]. Required weight of calcium carbonate slurry was taken in beaker and kept under agitation. Clay slurry and calculated amount of water were added to it to get targeted solid concentration. Starch paste was added slowly in pigment slurry to avoid any viscosity shock or lump formation. The speed of the agitator was lowered to avoid any foam formation during addition of synthetic binder. CS was then added slowly into the slurry. Lubricant, insolubilizer and synthetic thickener were added at the vortex after fixed interval of time. Finally OBA was added to the color. The pH of the color was adjusted to 8.5–9.0. The total solids of coating slip were kept around 50%.

The coating color containing various parts of CS with other ingredients was prepared as given in Table 2. Coating color formulation marked "control" was prepared without addition of CS. The parts of GCC and other additives were fixed throughout the experiments in all batches (marked as A to F).

2.5. Paper coating application

The coating color was applied to 21.0 cm \times 29.7 cm size base paper sheet using an automatic bar coater (K Control Coater, Model 101). The sheets were preconditioned for 24 h at 27 °C and 65% relative humidity. The coat weight was maintained around 13–14 g/m² with a thickness of 12–14 μm with bars used for applying the coating color on base paper. The coated sheets were immediately placed in an oven maintained at 105 °C for 60 s to dry. Coated paper was supercalendered in plant scale supercalender by applying a linear nip pressure of 76 bars at 50 °C. All the sheets were passed through single nip.

2.6. Characterization of coating and coated paper properties

Viscosity of coating color was measured on Brookfield viscometer (RVDV-II + Pro) as per Tappi Test Method T 648 om-97. Water retention value was measured on water retention meter (AA-GWR) as per Tappi Test Method T 701 pm-01. Basis weight of coated sheets was measured as per Tappi Test Method T 410 om-98. Thickness of coated sheets was measured on L&W thickness tester as per Tappi

Table 2
Coating color formulation.

Ingredients	Control	A	B	C	D	E	F
GCC	15	15	15	15	15	15	15
Clay	85	80	75	65	55	45	35
CS	0	5	10	20	30	40	50
Other additives	Constant						

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