Study on Improving the Opacity of Paper Using Adjunct Filler Pigments

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Keywords: Opacity, fillers, extender

Most writing and printing papers as well as many other paper and board qualities require high brightness and opacity to satisfy both the aesthetic and technical demands of carrying printed information. Sufficient opacity is important to prevent printed text from showing through on the reverse side of a paper. High brightness can be achieved by improved bleaching of pulp. However, opacity decreases with increase in brightness. Opacity of a paper can be increased with the help of filler loading. Some fillers like TiO_2, calcium carbonate, talc etc. can be loaded in paper to increase its opacity. TiO_2 being very expensive can not be used in all the grades of paper.

In the present work, some adjunct fillers/ filler extenders (both organic and inorganic) having good opacifying characteristics have been used in combination with calcium carbonate and talc. Effect of fillers on the optical properties (mainly on opacity) was studied. Three different filler extenders were evaluated for increasing the opacity. There was a significant change in opacity when these were used in combination with talc. But, the increment in opacity was not so significant when used in combination with very fine calcium carbonate.

INTRODUCTION

Most of the writing and printing papers require high brightness and opacity. High brightness provides a desirable contrast to the printed material while high opacity provides little or no 'show through' of printing on the reverse side of the sheet. Both brightness and opacity follow the well-known ,formulas of Kulbelka and Munk, and are dependent on the two coefficients of light absorption and light scattering [1]. The higher the scattering coefficient and lower the absorption coefficient, more opaque the paper sheet will be. In fact, when the light strikes on any object, it is reflected or transmitted or absorbed. The transmitted part of the light determines the opacity and transparency. The total transmitted light determines opacity.

Filler pigments are the materials, which are mainly used to get the desired optical properties of the paper with a comparatively low cost. The application of fillers is particularly important when opacity is needed at a low basis weight. There is certain limit to the amount of the filler pigment that can be added since these non-fibrous substances can adversely affect the strength, stiffness and other important physical properties of the sheets. For high opacifying power, a filler pigment should have high refractive index and fine particle size. White pigments such as calcium carbonate, titanium dioxide and zinc sulfide can be used for this purpose. Ground calcium carbonate is a common pigment for paper offering technical and economical advantages. Its high brightness often reduces opacity. This requires adding a pigment with high scattering coefficients [2].

To achieve high brightness and opacity with precipitated calcium carbonate (PCC), alkaline papermakers have been using a scalenohedral calcite. However, the papermaking objectives in wood containing and wood free paper are for even higher brightness and opaque sheets. This has led to the development of a new cost effective, high opacifying, high brightness PCC that competes with current high opacity fillers such as calcined clay and titanium dioxide [3]. Today, natural ground $CaCO_3$ (NGCC), recognized worldwide as a technologically advantageous and cost-effective paper filler and coating pigment, is used successfully in all continents. Neutral or alkaline papermaking, relying on the use of $CaCO_3$ is meanwhile being practiced successfully on a very wide scale [4].

Opacifying fillers or extenders are one of the options to get high opacity of paper. Generally having fine particle size and high brightness, it is used in a small quantity with major fillers (like calcium carbonate, talc, etc.) to increase the opacity of the paper than that can be achieved with major fillers only. The dose of the extenders is very small as compared to the dose of major fillers. Amongst all the opacifying fillers, the best known filler is TiO_2 as it has high reflectance, high refractive index, small particle size, non abrasive and chemically inert. Titanium dioxide pigments (TiO_2 pigments) are mainly used in paper products of high quality. The superior optical efficiency of TiO_2 pigments is manifested in lightweight grades, where high pigment loadings are prohibited by the inevitable deterioration in strength properties [5]. However, its high cost restricts its use for very few grades of paper and search for alternative options continues.

An organic pigment, Pergopak M2 is reported which imparts opacifying and brightening characteristics comparable to TiO_2 due to a high degree of light scattering [6]. In white paper, replacement of 20% TiO_2 by Zeolex 123, a sodium containing amorphous precipitated aluminosilicate increases brightness by over 7.5 units although opacity is slightly decreased. The effectiveness of Hydrex-P, magnesium containing amorphous precipitated aluminosilicate on properties of multiplayer board is greater than that of precipitated calcium carbonate [7]. The use of calcined clays in the paper industry has increased since the 1980's. Their main uses have been in coating applications to improve both offset and gravure printability, and as extenders or replacements for titanium dioxide pigment [8].

The objective of this study was to explore the feasibility of few low cost easily available extenders for improving the opacity of writing & printing papers with talc and calcium carbonate as major fillers.

EXPERIMENTAL

Materials

Three major fillers and three extenders were used in this study. The first one was Hydrocarb-60 (HC-60) (Honcal 1, supplied by IMERYS) which was calcium carbonate having 60% of total amount less than 2 micron particles. The specific gravity of HC-60 was 2.6-2.8 gm/cc and brightness of 96.1 % ISO. The second major filler was ground calcium carbonate (GCC) having brightness of 95.6% ISO. The third major filler was Finex (supplied by Gautam Mineral) which was nothing but talc, hydrated magnesium silicate with approximate formula $H_2Mg_3(SiO_3)_4$. Specific gravity was 2.75 gm/cc and brightness of 93.5% ISO. Water dispersions of filler (20 wt%) were used for dosing in the pulp slurry.

Three extenders, namely calcined clay, Hydrex-P and Paper filler were used. Calcined clay of 2.64 gm/cc specific gravity was supplied by English Indian Clays Ltd. Hydrex-P is the trade name of sodium magnesium aluminosilicate (supplied by J. M. Huber Corp.). It is a fine white powder, having a brightness of 100.0% ISO. The third one was organic pigment produced by Ciba-Geigy Ltd. It was based on a urea formaldehyde linear condensate polymer. It is available in the solid powder form, having a brightness of 99.2% ISO. The polymer was reported to have a refractive index similar to that of fibres and fillers in common use. Water dispersions of 5 wt% extenders were used for dosing in the pulp slurry.

For internal sizing, Ivax 2000 (from Ivax Paper Chemicals Ltd.) was used as the main sizing chemical at neutral pH. It was dispersed rosin with milky white appearance, anionic in nature having pH 6.5±0.5. Poly aluminum chloride (PAC) ECORITE-2018 (supplied by DCM Shriram Consolidated Ltd) having 16.6-17.5% Al_2O_3 was used for rosin precipitation and pH adjustment.

The cationic starch "PIRAAB" grade (from Global Technocrats Inc) with 10% moisture was used as retention aid. Starch solution of 1% concentration was prepared for addition to the stock.

Studies were conducted with a bleached pulp of mixed hardwood and bamboo, obtained from a large integrated pulp and paper mill.

Methods

Pulp was beaten to 30 °SR in the PFI mill manufactured by 'HAMJERN MASKIN as' controlled by Norwegian Pulp and Paper Research Institute as per Tappi standard T 248 sp00. All the experiments were conducted with bleached pulp refined to 30 °SR.

The hand sheets were made with 20g OD pulp according to TAPPI standard procedure (T 205 sp-02) with the following modifications. The sheets were made using pH adjusted dilution water. The pH of water was adjusted by PAC solution. The total volume of the slurry taken in the sheet former was around one litre.

The following sequence of addition of different ingredients of the stock was followed.

1. Beaten pulp
2. Opacifying filler
3. Major filler
4. Ivax 2000 (Neutral sizing chemical) - 25kg/T
5. PAC - 35 kg/T
6. Cationic starch - 10 kg/T

Experimental design

The experiments were planned to obtain 11% and 15% ash levels in the paper sheets. The following experiments were conducted:

1. First the ash optimization of major fillers was carried out. For that, 5 different dose levels [17,20,25,28,30%]

of Finex & 7 different dose levels of HC-60 [17,20,25,30,35,40,55%] were chosen.

2. To evaluate the improvement in optical properties, sheets were first made with opacifying fillers alone. Hydrex-P at 4 different dose levels [1,2,3,4%], Paper filler at 3 different dose levels [0.5, 0.75, 1 %] and Calcined clay at 5 different dose levels [1,2,2.5,3,4%] were evaluated.

3. As the extender dose level was negligible in comparison to major filler dose, the major filler dose level was kept constant to achieve a particular ash level in combination of major fillers and extenders.

4. For 11% ash level, the hand sheets were prepared from the following stock

Finex, 20% + Hydrex-P [1%, 1.5%,2%]
Finex, 20% + Paper Filler [0.5%, 0.75%, 1 %]
Finex, 20% + Calcined clay [1%, 2%, 3%]
HC-60, 35% + Hydrex-P [1%, 1.5%,2%]
HC-60, 35% + Paper Filler [0.5%, 0.75%, 1%]
HC-60, 35% + Calcined clay [1%, 2%, 3%]

5. For 15% ash level, the hand sheets were prepared from the following stock.

Finex, 28% + Hydrex-P [1%, 1.5%,2%]
Finex, 28% + Paper Filler [0.5%, 0.75%, 1%]
Finex, 28% + Calcined clay [1%,2%,3%]
HC-60, 55% + Hydrex-P [1%, 1.5%,2%]
HC-60, 55% + Paper Filler [0.5%, 0.75%, 1%]
HC-60, 55% + Calcined clay [1%, 2%, 3%]

Testing/ analytical methods

The extent of refining of pulp, °SR, was determined as per ISO 5267-1: 1999. The ash content of hand sheets was determined according to TAPPI standard T 211 om-93.

Hand sheets were conditioned according to TAPPI standard (T 402 sp -98) at 23±1°C and 50±2% relative humidity for 4 hours before testing. The brightness tester (Technibrite Micro TB 1 c) was calibrated with primary standard and swing in standard. Then different optical properties were measured with this instrument following TAPPI standards: TAPPI Test method T 525 om-02 for brightness; T 519 om-02 for opacity; T 519 om-02 for scattering coefficient and T 560 om-96 for whiteness.

RESULTS

Two types of ground calcium carbonate (Hydrocarb-60 and GCC) and talc (Finex) have been studied at different ash levels for opacity improvement. Hydrocarb-60 shows highest brightness (96.1% ISO) and CIE whiteness (98.5) followed by GCC and Finex as shown in Table 1. Hydrocarb-60 has finer particle size compared to GCC and Finex. The fraction below 2.2 micron in case of Hydrocarb-60 was 78.4% whereas it was 20.9% and 11 % in Finex and GCC respectively. All the major fillers were water insoluble and their 20% slurry showed pH in alkaline regime (Table 1).

Further studies were conducted with Hydrocarb-60 and Finex because GCC could not give significant opacity improvement due to its course size. Calcium carbonate (Hydrocarb-60) and talc (Finex) were loaded in paper for two different ash levels (11% and 15%) in hand sheets. Finex gave 11% ash at 20% dosing and 15% ash at 28% dosing whereas Hydrocarb-60 gave the corresponding ash levels at 35% and 55% dosing respectively. The retention of Hydrocarb-60 was much lower compared to Finex. The first pass ash retention (FPAR) was 38-40 % for Hydrocarb 60 and 62-64% for Finex.

Both inorganic and organic types of adjunct fillers/ extenders (opacifying fillers) were studied at different dose levels and finally the superior extenders are loaded at their optimized dose separately with the two major fillers. Among the extenders, Hydrex-P showed highest brightness, 100.0% ISO followed by Paper filler, 99.2% ISO and calcined clay, 93.5% ISO (Table 2).

With the increase in Hydrex-P dose, there was a uniform increment in all the optical properties. The opacity increment at 1,2,3 and 4% dose levels were 0.8 unit, 1.4 units, 2.0 units and 3.3 units respectively. Finally, 2% dose of Hydrex-P was selected for further studies. With calcined clay, the maximum increment in opacity (1.8 units) was noticed at 3 and 4% dose levels.

In case of Paper filler, maximum increment of 1.3 units in opacity was obtained at 0.75 % dose level.

Table 1 : Physical and optical properties *of* major fillers

Properties	Finex	GCC	Hydrocarb-60
Brightness, %ISO	93.5	95.6	96.1
CIE Whiteness	90.9	97.6	98.5
Color	white	white	white
pH (20 % slurry)	7.95	8.25	8.70
Solubility in water	insoluble	insoluble	insoluble
Moisture, %	0.09	0.06	0.23

Table 2 : Physical and optical properties *of* extenders

Properties	Hydrex-P	Paper filler	Calcined clay
Brightness, % ISO	100.0	99.2	93.5
CIE Whiteness	105.2	102.6	94.1
Nature	amorphous	amorphous	amorphous
Colour	white	white	white
pH (5 % slurry)	7.10	8.68	6.51
Solubility in water	insoluble	insoluble	insoluble
Moisture, %	1.50	7.57	1.93
Nitrogen content, %	nil	34.56	nil

With Finex

Finex at 11 % loading could increase the opacity and scattering coefficient by 1.1 and 2.0 units when used alone. In combination with Hydrex-P, Paper filler and calcined clay, there were additional increments of 1.7, 0.1 and 1.3 units in opacity (Fig. 1) and 1.1, 0.3 and 1.0 unit in scattering coefficient (Table 3). At 11 % ash level with Finex alone, brightness increment was 0.6 unit from blank, whereas in combination with Hydrex-P, Paper filler and calcined clay brightness further increased by 0.7 unit, 0.1 unit and 0.2 unit respectively. With Finex alone, CIE whiteness increased by 1.5 units from blank, whereas in combination with Hydrex-P, Paper filler and calcined clay there were further increments of 1.5 units, 0.3 and 0.5 unit respectively.

Finex at 15% loading could increase the opacity and scattering coefficient by 1.5 and 2.6 units when used alone. In combination with Hydrex-P, Paper filler and calcined clay there were additional increments of 2.5, 0.2 and 1.7 units in opacity (Fig. 1) and 2.8, 0.1 and 1.3 units in scattering coefficient (Table 4). At 15% ash level with Finex alone, brightness increment was 1.6 units from blank, whereas in combination with Hydrex-P and calcined clay brightness further increased by 0.7 unit and 0.3 unit, Paper filler gave no more increment in brightness. With Finex alone, CIE whiteness increased by 1.7 units from blank, whereas in combination with Hydrex-P, Paper filler and calcined clay there were further increment of 1.7 units, 0.4 and 1.6 units respectively.

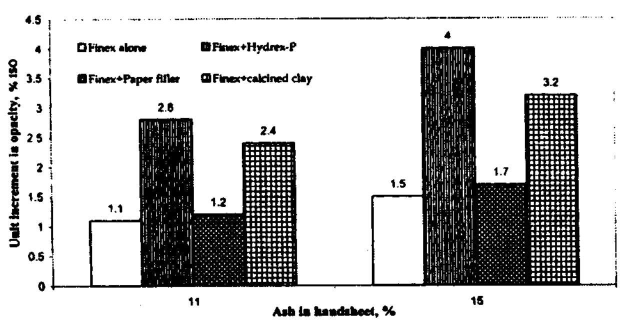

Figure 1 : Effect of extenders on opacity in combination with Finex as filler

Table 3 : Effect *of* extenders on optical properties in combination with Finex at 11% ash level

Parameter	Blank	Finex	Finex dose, 20 %		
		Hydrex-P	Paper filler	Calcined clay	
Filler dose, %		20	2.0	0.75	3.0
Brightness, % ISO	83.4	84.6	84.7	84.1	84.2
CIE Whiteness	73.6	75.1	76.6	75.4	75.6
Opacity, % ISO	74.2	75.3	77.0	75.4	76.6
Scatt. coeff, m^2/kg	26.69	28.69	29.79	28.99	29.69
FPAR, %	-	62.35	62.35	61.50	60.89

Table 4 : Effect of extenders on optical properties in combination with Finex at 15% ash level

Parameter	Blank	Finex	Finex dose, 28 %		
			Hydrex-P	Paper filler	Calcined clay
Filler dose, %		28	2.0	0.75	3.0
Brightness, % ISO	83.4	85.1	85.7	85.0	85.3
CIE Whiteness	73.6	75.3	77.0	75.7	76.9
Opacity, % ISO	74.2	75.7	78.2	75.9	77.4
Scatt. coeff, m^2/kg	26.69	29.29	32.09	29.40	30.59
FPAR, %	-	64.72	66.21	66.20	62.60

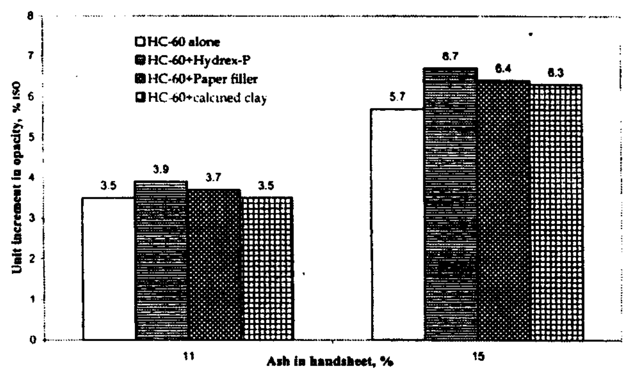

Figure 2 : Effect of extenders on opacity in combination with Hydrocarb-60 as filler

With Hydrocarb-60

The effect of Hydrex-P, Paper filler and calcined clay in combination with Hydrocarb-60 at 11% level is given in (Table 5).

With Hydrocarb-60 alone at 11% loading, opacity and scattering coefficient increments were 3.5 and 7.1 units respectively, whereas in combination with Hydrex-P opacity increased further by 0.4 unit and scattering coefficient by 1.3 units. The brightness and whiteness also increased by 1.9 and 3.9 units respectively, whereas in combination with Hydrex-P brightness further increased by 0.4 unit and whiteness by 0.5 unit.

In combination with calcined clay, although brightness increased by 0.4 unit and whiteness by 0.3 unit but there was no more increment in opacity and scattering coefficient. Again in combination with paper filler, there were no additional increment in brightness, whiteness, opacity and scattering coefficient. The effects on opacity are shown in Fig 2.

Hydrocarb-60 at 15% loading could increase the opacity and scattering coefficient by 5.7 and 10.3 units when used alone. In combination with Hydrex-P, Paper filler and calcined clay there were additional increments of 1.0, 0.7 and 0.6 units in opacity (Fig. 2) and 2.0, 1.6 and 1.2 units in scattering coefficient. With Hydrocarb-60 alone at 15 % ash level, brightness increment was 3.5 units from blank, whereas in combination with Hydrex-P, Paper filler and calcined clay no additional increment in brightness was noticed. CIE whiteness increased by 6.3 units from blank, whereas in combination with Hydrex-P, Paper filler and calcined clay there were further increments of 0.5 unit, 0.7 unit and 0.3 unit respectively (Table 5 & Fig. 2).

DISCUSSION

At the same ash level, Hydrocarb-60 showed higher increment in opacity as well as in brightness due to its smaller particle size (78% less than 2 micron) and higher brightness in comparison to Finex which has only 11% particles less than 2 micron in size. To obtain the same ash content in hand sheets, dosing of Hydrocarb-60 has to be around 1.5 times compared to that of Finex due to lower retention of Hydrocarb-60. Very small particle size of Hydrocarb-60 seems to be responsible for its low retention.

Hydrex-P gave the highest increment in opacity and scattering coefficient as well as in brightness & whiteness, in combination with Finex compared to other extenders. The opacity increments were 2.8 and 4.0 units at 11% and 15% ash levels compared to blank.

Finex-calcined clay combination could increase the opacity by 2.4 and 3.2 units at 11% and 15% ash levels compared to blank. In fact, during the calcination of clay, the hydroxylation water is first driven off at 500-700 °C and on continuous heating to 900-1000 °C, the particles start fusing together into secondary particle aggregates and further agglomerates to tertiary particles. End result is a large number of clay air interfaces and relatively high internal pore volume hence increasing light scattering & opacifying properties.

Finex-Paper filler combination could not provide good opacity, the reasons for the same are not very clear although these types of compounds are known to increase the opacity.

The effect of extenders was not so significant with Hydrocarb-60. This may be due to the fact that Hydrocarb-60 itself has fine particle size, giving high

Table 5 : Effect of extenders on optical properties in combination with Hydrocarb-60 at 11 % ash level

Parameter	Blank	HC-60		HC-60 dose, 35 %	
			Hydrex-P	Paper filler	Calcined clay
Filler dose, %		35	2.0	0.75	3.0
Brightness, % ISO	83.4	85.3	85.7	85.5	85.7
CIE Whiteness	73.6	77.5	78.0	77.5	77.8
Opacity, % ISO	74.2	77.7	78.1	77.9	77.7
Scatt. Coeff, m^2/kg	26.69	33.79	35.09	33.98	33.94
FPAR, %	-	40.19	40.99	40.47	40.37

opacity and scattering coefficient.

CONCLUSION

Hydrocarb-60 is very good filler for neutral and alkaline papermaking to increase opacity and brightness. It can increase paper opacity up to 5 units when used alone. Effect of extender is not appreciable in combination with HC-60. However, its retention is rather poor.

Hydrex-P is one of the best opacifying filler pigment. Finex & Hydrex-P combination gives very good improvement in opacity. It may be further improved by optimizing the dose of Finex and Hydrex-P. Finex & calcined clay combination also gives some increment in opacity. Paper filler in combination with Finex is not giving much increase in the opacity of paper.

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Table 6 : Effect of extenders on optical properties in combination with Hydrocarb-60 at 15% ash level

Parameter	Blank	HC-60		HC-60 dose, 55 %	
		Hydrex-P	Paper filler	Calcined clay	
Filler dose, %		55	2.0	0.75	3.0
Brightness, % ISO	83.4	86.9	87.0	87.1	87.0
CIE Whiteness	73.6	79.9	80.4	80.6	80.2
Opacity, % ISO	74.2	79.9	80.9	80.6	80.5
Scatt. Coeff, m^2/kg	26.69	36.96	39.12	38.57	38.16
FPAR, %	-	39.36	40.03	39.64	40.21