Use of Calcium Carbonate as Filler with ASA A-Successful Story at Bilt-Ashti

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ABSTRACT

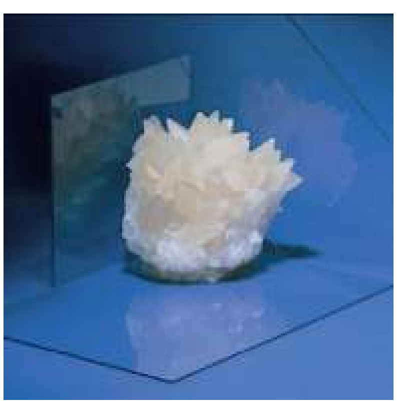
Ballarpur Industries Ltd.Unit-Ashti is located in dense forest covered area in Gadchiroli district of Maharashtra. In search of an opportunity to explore further Quality Improvement Strategy on branded products & comparing with that of leading competitors, The Unit-Ashti of Ballarpur Industries Ltd. has dared to dream about first ever Paper manufacturing entity to go with ASA sizing along with PCC (Precipitated Calcium Carbonate) in copier segment in India.

In line with conventional paper making in India, Mill was operating with Soap Stone till second quarter of 2007-08 with ASA sizing. Due to degradation in the quality of the soap stone powder received on site vis-à-vis cutting problems in final product, decision was taken to replace it with GCC (Ground Calcium carbonate) for sustenance of Quality, specially on smooth cutting of paper. To add up the beauty to the new knowledge gained with GCC on Quality front, Unit has beget new questions in search of improved answers further on Quality front with the help of PCC in line with international bench marking in paper making, First ever in Paper making Industry, in India. This Paper deals with introductory value additions on GCC & benefits derived by replacing GCC with PCC at the end. Hunger to conserve energy has recently won the**"Certificate of Merit"** in **"National Energy Conservation Awards" for the Year 2007.**

Calcium Carbonate is an exceptional mineral. The chemical formula CaCO3 covers a raw material, which is widespread throughout nature, whether dissolved in rivers and oceans, in molten form as "cold" carbonated-lava, or solid as a mineral in the form of stalactites, stalagmites or as the major constituent of whole mountain ranges. Plants and animals need calcium carbonate to form their skeletons and shells. The Earth's crust contains more than 4% calcium carbonate. As a result, the three calcium carbonate minerals - calcite, aragonite and vaterite - are among the most important rock-forming minerals. Rocks are not the only calcium carbonate deposits in nature, most stretches of water and countless plants and animals contain huge amounts of calcium carbonate. The link between these natural resources is the calcium carbonate cycle. Plants and animals absorb calcium carbonate from water - where it exists, in most cases, in the dissolved form of calcium hydrogen carbonate Ca(HCO3)2 - and use it to build up their skeletons and shells. After their death, crustacean, coccoliths, algae and corals form sedimentary deposits on sea-beds, thus the rock forming process is put in motion. The first stage is the sedimentation process from which chalk and limestone originate. Chalk is a poorly compacted sedimentary calcium carbonate rock, whose digenesis is incomplete. When the sedimentation process is completed this results in the formation of limestone.

If the sedimentation process takes place in magnesium containing water a dolomitisation may occur. Part of the calcium ions in the crystal lattice are replaced by magnesium ions, a fact that leads to the formation of dolomite CaMg[CO3]2. The carbonate rocks, chalk, limestone, dolomite and marble rocks are subject to erosion, under the influence of wind, temperature and water they dissolve, and the cycle may start again.

Multiple properties manifold uses



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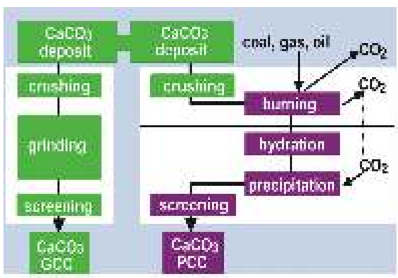
Paper: Over the last 30 years, the use of calcium carbonate has grown significantly as technology in the paper industry has moved from acid to neutral sizing. Today, calcium carbonate is the most widely used mineral in paper-making. GCC and PCC are used both as a filler and a coating pigment, and help produce papers with high whiteness and gloss and good printing properties.

Natural **G**round **C**a**C**O3 (**GCC**) is used successfully on all continents. At present, Europe is the one with the highest supply density (production sites and strategically located tank farms for slurry distribution). Limestone, marble and to a lesser extent chalk, are used as source material.

The amount of fine paper produced under alkaline conditions, using CaCO3 for best results has increased rapidly over the past few years. In Europe more than 95 %, in North America about 75 % of woodfree coated and uncoated papers were made alkaline in 1994. The advantages of alkaline papermaking are mainly derived from the absence of significant amounts of alum and acid pH values, and the use of GCC as a primary and/or via coating as secondary filler. In Europe, AKD is successfully used as alkaline sizing agent in the furnish and holds more than 90% of that market. Obtaining desirable high first pass retention is facilitated by a broad choice of different retention systems available today. Modern multi-component retention systems allow mills to reach good and stable retention values at still acceptable formation. Practical recommendations are offered to minimize potential wire wear, associated with the use of fillers. A potential formation of white pitch can be prevented by applying low mw cationic polymers.

Process of Manufacturing

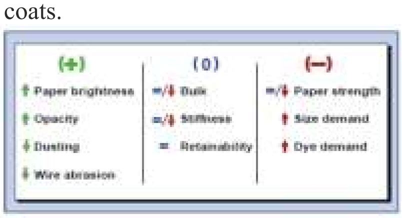


Product Characteristics and Delivery Forms

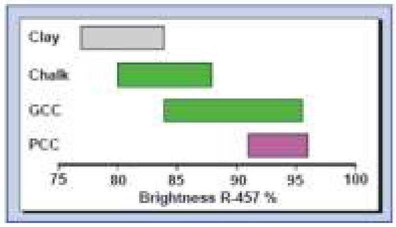
Depending on its requirements, the paper industry can choose from an available brightness spectrum of 80 - 96% Elrepho. Obviously this higher pigment brightness was one major factor making mills switch from clay to GCC . Particle sizes of the products range from 40 - 98 % below 2 microns. Finenesses of filler carbonates (anionic or cationic wet ground) for uncoated papers and coating base stock start at 40% and extend up to 90 % below 2 microns.

Natural Fillers for the Paper Industry

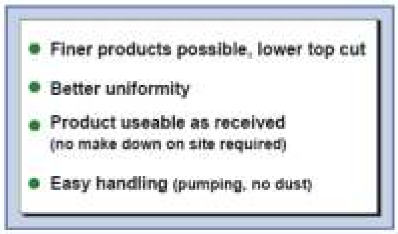
The effects on major properties of fine vs. coarse GCC/PCC fillers are presented in Fig below. For Un-coated papers, qualities with a fineness of 60 % below 2 microns are preferred. The finest 3 qualities with up to 90 % below 1 micron are used for single and top coats.



Its high natural brightness enables the user to cut down on the amounts of fibre bleaching agents and optical brighteners.



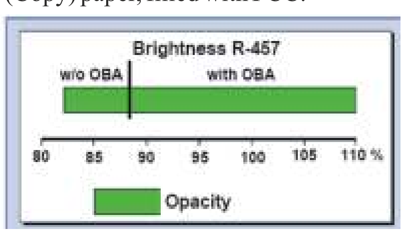
Slurries offer a number of advantages, quality wise and with respect to handling (See Fig.). This is therefore by far the most dominant PCC delivery form.



Slurry concentrations depend on fineness and end use and are offered in a range from 65 - 78 %. Most of these slurries are anionically dispersed. The technology of cationic wet grinding of CaCO3 filler slurries and their stabilization is in place.

- **BRIGHTNESS**

The effectiveness of the normally anionic oriented optical brighteners is intensified in the alkaline environment. OBA savings of up to 80 % over the acid system have been realized by alkaline paper mills, using high brightness natural ground CaCO3 (marble) as filler. In light of present-day environmental awareness (AOX/ adsorbable organic halogen, optical brighteners), interest in using high brightness natural ground CaCO3 products for the manufacture of papers having a high "natural" brightness, is gaining ground. Fig. Provides an overview on brightness and opacity of (Copy) paper, filled with PCC.

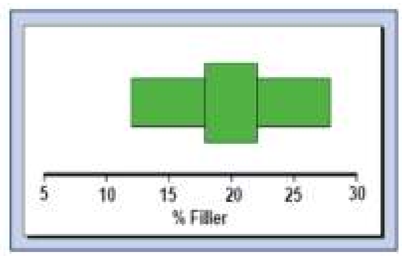


- **STRENGTH**

There is a tendency towards higher paper strength when running alkaline without high amounts of Al2(SO4)3. This allows the papermaker depending on the previous acid conditions and the basic fibre composition, to raise the filler loading by 1 - 5 % points and still retain the same paper strength. This potential is a by-product of more favourable refining conditions (slightly alkaline, low salt load) and the absence of aluminium compounds in the paper. Other contributing factors are potentially higher starch retention in the wet end and starch receptivity in the size press. In general, it is always interesting for the papermaker to increase the filler level. However, there are also limitations.

Filler Loading Increase Advantages and Limitations

Using 80 g/m[2] copy paper as an example, filler loadings presently practiced in Europe are shown in Fig. They range from 12 - 28 % with the bulk of the copy papers being PCC filled at levels between 18 - 22 %.



- **REFINING**

Slightly alkaline pH-values and a low salt load are the reasons for a relatively lower energy demand in refining compared to acid refining. According to literature energy savings up to 30 % have been recorded. Adjustment for porosity (lowering) via higher degree of refining can however reduce this advantage.

- **DRAINAGE, DRYING**

An explanation for the more favourable drainage and drying properties, as we see it, is the absence of aluminium hydroxide complexes in the fibrous web and the presence of natural ground CaCO3 as filler. Compared to the platelet shaped clay, a more open paper structure (micro porosity) is created by the rhombohedral particles of natural ground CaCO3. Natural carbonate by itself is considered to be more hydrophobic than clay. For that reason, there is no need for evaporation of "inherent moisture" from the pigment. The afore-mentioned advantages can be translated into steam savings and/or production increases (speed).

- **WATER**

Because of their lower electrolyte load, alkaline systems allow a tighter circuit closure. Positive consequences thereof are higher circuit water temperatures (better drainage, lower bacteriological activity) and reduced specific fresh water demand.

- **pH STABILITY**

Owing to its strong buffering action, natural ground CaCO3 keeps pH-values of the system on a stable level in the range of 7.2 to 8.4.

- **RETENTION**

The aim of a high first pass retention FPR is to immediately retain all furnish components and to prevent any critical concentrations of fines, additives and their decomposition products in the water circuit. Furthermore, a high FPR improves runnability, wire and felt life and reduces defects in the paper.

How good a retention including acceptable formation is achieved, depends very much on a careful balance of the whole wet-end chemistry. Laboratory tests at the mill site can be of indicative value. However, mill trials under mill specific conditions, carefully planned to furnish vital data, are indispensable.

Sizing with ASA

- **ASA Alkenyl Succinic Anhydride**

ASA needs to be emulsified at the paper mill prior to its application. This is being done by using special equipment (shear forces) and applying cationic starch (mostly potato) or a synthetic polymer. The usual ratio cationic starch/ASA is about 4:1. The addition rate depends on the system given and the required sizing degree. The addition level necessary to attain the desired degree of sizing can be adjusted more easily and more precisely than is the case with AKD.

ASA reacts particularly fast with the OH groups of the fibers, but does so also with water. With ASA sizing prior to the size press is already 80 - 90 % developed. Particularly in the past, the fast hydrolysation characteristic was identified as the source of holes, spots and the cause of runnability problems in a number of mills. Hydrolysed ASA (dicarbonic acid) together with Ca or Mg ions can form stickies which deposit in the approach flow, on wires and felts or predrier doctor blades. To minimize this potential problem one needs to optimize the system, operate at high first pass retention and avoid breaking of the emulsion.

ASA not retained is easily susceptible to hydrolysation. Hydrolysed ASA actually can have a desizing effect. ASA suppliers usually recommend the use of some alum added to the thin stock to further improve retention. ASA like AKD reduces toner adhesion more than rosin sizing. ASA is claimed not to cause the kind of slipperiness of the paper which can be experienced when AKD is used.

MILL EXPERIENCE (RESULT & DISCUSSION)

I. CONVERSION TO GCC FROM SOAP STONE POWDER (With ASA alkaline Sizing)

Initial trials started in September 2007 with partial quantities and 100% GCC. Trials were successful with regard to quality improvement, elimination of conversion problems and positive feedback from customers.

OBSERVATIONS

- Strength properties remained same as compared to properties of paper manufactured with Soap Stone Powder.
- Opacity increased by three points.OWA consumption is reduced by 25% due to higher brightness of GCC. ASA consumption is increased by 35-40%.

RDA'S(Retention & Drainage Aids)

Percol dosing increased by 100%..
Hydrocol addition increased by 20%.
Addition of Soda ash stopped and dosage of PAC reduced to control pH (Table on Next Pages).

Advantage gained in branded product- COPY POWER, with GCC Filler over SS Powder

GCC filler and ASA Alkaline sizing in the manufacture

Paper Properties: New improved

1. Finer & sharper cut quality of the product.
2. Brightness visual appeal enhanced a stable shade / brightness of paper.
3. Opacity of the paper increased see through improved significantly.
4. Improvement in physical appeal of paper with good stiffness.
5. Uniformity on the surface of the sheet.
6. Elimination of fluff and cutting dust generation.
7. Anti-fading paper with no color reversion due to alkaline sizing.
8. Acid free paper due to ASA alkaline sizing.

Advantage of COPY POWER on performance

Enhanced results for the customer: Photocopying properties

1. Better toner adhesion with improvement in sharpness of the image after photocopying.
2. No see through & good back to back copy. No dust / Fluff accumulation in photocopying machine.
3. Smoothly running paper on high speed photo copier machines flat & Jam free performance.
4. Permanence of copied paper document preserved over years.

FROM GCC TO PCC (ASA Alkaline Sizing with PCC) A TRIAL

OBSERVATIONS(Refer Annexures)

- Back water hardness increased from 80 ppm to 220 ppm.Conductivity increased from 600 to 1100 micro mhos.
- Back water pH remained at the same level with in the range of 7.8 8.0.
- Back water alkalinity increased from 100-120 to 140-150 ppm.
- Turbidity increased from 26 to 300 NTU. FPR & FPAR maintained at same levels with a marginal

reduction in RDA chemicals. Pigmented dye consumption increased by about 20%.

- ASA consumption increased by 15-20%.Marginal/No reduction in OBA consumption.
- Gain in Opacity by one point. Stiffness values are same.
- Machine runnability disturbed every time during increase in PCC content due to formation of deposits in the system. Machine requires frequent cleaning increasing the downtime.
- Paper properties of BCP grade are maintained even after complete elimination of BCTMP.
- BCTMP street can be eliminated which will give a major gain on energy consumption (Shark Pulper, pump and agitator in chest, Deflaker, pump and agitator in chest and steam consumption for processing BCTMP)

CONCLUSION

Today, wood free papermaking at neutral to slightly alkaline pH-values is a world-wide well established technology. Whatever conversions from acid to alkaline still remain, they can benefit from a vast body of experience. Papermakers and raw material suppliers as well as research institutes should keep on working towards further optimizations.

New knowledge thus gained will always beget new questions in search of an answer - **which is what progress is built on.**

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Annexure-1

Comparative benefits vis-a-vis GCCVs PCC can be summarized as below;

PARTICULARS	GCC	PCC
Drainage on wire	+ (high)	- (low due to spiky shape and higher surface area
Steam consumption	+ (low)	- (High)
Brightness	+	- No gain in OBA in spite of higher brightness of filler (97%)
Opacity	+	+
Strength Properties	No loss on increase of ash	Loose strength properties on higher ash content
Bulk	No increase (support of BCTMP required)	Increases bulk itself
Smoothness	Calendar loading is required	Gives a very smooth sheet at min. loads
Wet end chemical consumption	Low	High

Major Quality Improvements

Sl. No.	Property	Product prior to Oct'2007 (With Soap Stone)	Product post Oct'2007 (with GCC)
1	Brightness	Lower	Higher due to higher filler brightness
2	Opacity	Lower	Higher
3	Whiteness	Lower	Higher
4	Shade	Less stable	Stable
5	Ageing	Drop in strength & color reversion	Strength stability & no color reversion
6	Dusting	High	Comparatively low
7	Smoothness	Low comparatively	Good hand feel
8	Refractive Index	Low	High

Annexure-3

Comparison of Wet end parameter in SS Powder,GCC & PCC

Sl.No	Property		UOM	SS Powder	GCC	PCC
1	Head Box	CY	%	0.56 – 0.58	0.58 – 0.64	0.56 – 0.61
		°SR	°SR	22 – 23	22 – 26	22 – 25
		Drainage	--	550 – 560	580 – 630	580 – 610
		Charge Demand	Meqv/k/lit	-14 to -12	-17 to -7	-7 to -6
2	Back Water	CY	%	0.11 to 0.12	0.09 - 0.13	0.09 - 0.11
3	FPR		%	79.0 – 79.9	79.0 – 84.2	82.9 – 83.9
4	FPAR		%	48.7 – 50.3	48.0 – 53.6	51.8 – 52.9
5	Alkalinity		Ppm	80 – 90	100 – 120	140 – 150
6	Hardness		Ppm	50 – 70	60 - 80	180 – 220
7	Conductivity		Micro mhos	500 – 650	500 – 650	950 - 1100

Annexure-2

Major Comparison of SSP, GCC & PCC Filler

Sl. No.	Property	SS Powder	GCC	PCC
1	Particle size	05 to 15 Micron	60% < 02 Micron	3.5-4.0 Micron
2	Abrasion Index	High due to higher particle size and impurities	Lower as compared to SS Powder due to lower particle size higher purity	Lowest as compared to SS Powder and GCC
3	Brightness	90+	94+	97-98
4	Filler handling	Cost involved & Dust pollution	Ready to use as received in liquid from from our own company	Available both in powder and liquid form
5	Brightness	More OWA required to achieve desired brightness	OWA consumption reduced due to higher brightness of GCC	OWA consumption remained same
6	Opacity	Low comparatively	Higher	Higher
7	Dusting	High	Very Low	Comparatively very Low
8	Smoothness	Low comparatively	Improved smoothness	Good hand feel and highly smooth surface
9	Refractive index	Low	High	High

Annexure-4

Comparison of paper properties in SS Powder,GCC & PCC

Details		UOM	BCP With SS Powder			BCP With GCC			BCP With PCC		
			Min	Max	Average	Min	Max	Average	Min	Max	Average
Substance		gsm	74.5	76.5	75.7	73.5	77.2	75.4	74.3	76.5	75.5
Thickness		microns	105	110	109	109	111	110	109	111	110
Brightness		% ISO	90	90.91	90.58	89.78	91.39	90.5	90.8	92.2	91.5
Opacity		% ISO	92.5	94.4	93.4	93.7	95.6	95.0	94.4	96.1	95.7
Smoothness	TS	ml/min	263	314	290	255	331	303	140	270	210
	WS	ml/min	320	361	337	331	396	366	160	290	230
Ash %		%	13.41	14.01	13.68	12.20	16.00	13.99	11.82	14.15	13.26
Tear Factor	MD	-	57	59	58	54	59	57	58	63	61
	CD	-	63	64	64	58	65	62	65	69	67
Br. Length	MD	mtr	4367	5067	4695	4222	4872	4588	4605	5145	4875
	CD	mtr	2224	2586	2463	2048	2422	2278	2305	2675	2460
Stiffness	MD	Taber	2.63	2.67	2.64	2.63	2.66	2.65	2.64	2.74	2.67
	CD	Taber	1.60	1.65	1.63	1.62	1.65	1.63	1.61	1.65	1.63
Waxpick	TS	No	14	14	14	14	14	14	14	14	14
	WS	No	14	16	16	14	14	14	14	14	14