Precipitated Calcium Carbonate (PCC)

1. Introduction

Limestone is a common type of sedimentary rock in the earth's crust which primarily constitutes of $CaCO_3$.

Calcium carbonate ($CaCO_3$) is the most widely used filler and/or extender material in paper, paint, plastic, sealant, adhesive, food, ceramic, textile (carpet), cosmetics, medicine, and several other industries. Each industry requires specific product characteristics in terms of chemical purity, particle size distribution, shape and surface area, whiteness, and rheological behavior, etc.

There are two types of calcium carbonate powder, namely ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC) in the world.

1.1. Ground Calcium Carbonate (GCC)

GCC is extracted from the earth and is present in varying quantities in the form of calcite, aragonite, vaterite, limestone, chalk, marble or travertine. Ground calcium carbonate commonly referred to as GCC and is widely used as an industrial mineral. Following its extraction, GCC is ground either under dry or wet conditions depending on the final product requirements. Ground Calcium Carbonate (GCC) differs from Precipitated Calcium Carbonate (PCC) in that the GCC is formed directly from grinding limestone rock into a powder, while PCC is chemically produced and precipitated out as powder.

1.2. Precipitated calcium carbonate (PCC)

Calcium carbonate ($CaCO_3$) is abundantly present on the earth. Natural, ground or synthetic $CaCO_3$ is widely used in various industries. The product, produced by a controlled synthesis to fulfill the desired properties is called precipitated calcium carbonate (PCC). It is also called as synthetic, refined or purified $CaCO_3$. PCCs have the same chemical formula as of its natural resources limestone, chalk, and marble; $CaCO_3$. PCCs gain advantages over natural and ground $CaCO_3$ with their unique properties of submicron particle size, regular crystal shape, narrow particle size distribution, and high purity.

Unlike ground $CaCO_3$, PCCs can be produced in different crystal shapes and ultrafine particle sizes.

Commercial PCCs have been made for a long time since 1841. The first producer was the English company, John E. Sturge Ltd., which treated the residual $CaCl_2$ from their $kClO_3$ manufacture with Na_2CO_3 and CO_2 to form what they called precipitated chalk. In 1898, a new factory was built in Birmingham using the milk of lime process, which is described in more detail below. PCC production in the U.S. dates from 1938, when the C.K. Williams Company in Adams, Massachusetts, began to make PCC using the limestone from their adjacent mine.

The minerals also can be produced by a chemical process, namely lime soda process, calcium chloride process and carbonation process

Table 1: Typical physical properties of a PCC product [3]

Physical Properties	
Crystal Structure	Calcitic
Water Absorption	80 to 85 ml/100 g
Oil Absorption	60 to 65 ml/100 g
Loss on Drying at 105 ºC	0.8 % Max.
Specific Gravity	2.6 to 2.7
Bulk Density	0.45 to 0.50 g/cm3
Average Particle Size	3 to 5 µm
Residue on 300 mesh	0.2 % M

PCC in nature can be obtained in three main crystal polymorphs: calcite (rhombohedral), aragonite (orthorhombic), and vaterite (hexagonal) depending on the reaction conditions and impurities in the process. Calcite is the most thermodynamically stable under ambient conditions, but other polymorphs can form under specific kinetic conditions. Aragonite is more soluble and denser than calcite. It usually forms needle-like orthorhombic crystals and is favored at high temperatures and pressures. It is met stable, converting slowly to calcite. Vaterite is the thermodynamically least stable polymorph and its hexagonal crystals are rarely seen in the naturally occurring mineral [1, 2, 3, 4].

2. Process Description (PCC)

2.1. Limekiln (Calcination process)

In the first step of the plant, the limestone is converted into lime in a lime kiln. heating temperatures between 800 C^0-1100 C^0 is required. At these temperatures, the limestone breaks down by giving off carbon dioxide and leaving as calcium oxide which is known as quicklime.

$$CaCO_3 \text{ --> } CaO + CO_2$$

2.2. Milk of lime preparation

In the second process step, the lime is fed from the quicklime silo to the wet lime slaker. Inside the slaker, the lime reacts with a defined amount of water to calcium hydroxide slurry.

The chemical reaction during lime slaking:

$$CaO + H_2O \text{ --> } Ca(OH)_2\text{+heat}$$

The quantity of hydrated lime and water volumes fed to the slaker are carefully measured through a precise dosing system aiming at constantly obtaining milk of lime at the request density.

The slaker is a closed mixing tank, where water and lime can react continuously in a defined proportion. The following screening step removes undesired grits (unburnt, unreacted particles) from the hydroxide slurry. Then the slurry is transferred to the carbonator.

2.3. Carbonation and gas treatment

In this section, the calcium hydroxide slurry is transferred to carbonators, where the calcium hydroxide reacts with carbon dioxide to calcium carbonate (PC).

The chemical reaction during PCC production:

$$Ca(OH)_2 + CO_2 \text{ --> } CaCO_3\text{+}H_2O\text{+heat}$$

The required CO_2 is taken from the vertical shaft kiln through a connecting pipe.

2.4. Drying station

From the carbonator, the PCC slurry is pumped to the storage with an agitator. From there the slurry is pumped to the filter press. The PCC cake then is moved by a special screw feeder into a high-efficiency drying system, special design for PCC, in which PCC particles are dried and kept separated one from the other.

2.5. PCC screening, storing and packing

After being dried, the PCC is screened then transferred to the storage silos where it is fed to the packaging plant.

2.6. Coated PCC production line

The surfaces of the PCC particles are often coated with a low percentage of a fatty acid layer, such as stearic acid, or other organic material, for use in non-aqueous systems. The choice of the coating depends on the type of polymer. the PCC will be used in and the performance desired. These coatings increase the dispersibility of the PCC in the polymer or solvent as well as its compatibility with the polymer or solvent, which in turn increases the performance and efficiency of the PCC.

3. Crystal Structures and Size of PCC

The following SEM pictures are showing the different morphologies that can be generally produced in a PCC plant. There are four basic crystalline forms of PCC crystals. There is aragonite, rhombohedral, scalenohedral, and prismatic. Calcite is the most stable form of calcium carbonate.

A summary of the physical properties of other PCC morphologies can be found below in table 2.

Table 2: Summary of PCC properties [5, 6].

Morphology	Specific Surface Area (m^2/g)	Refractive Index	Brightness(%)	Particle Size (µm)	Einlenhner Abrasion (mg)
Rhombohedral	2-10	1.58	99	0.2-1.3	2-4
Scalenohedral	5-25	1.58	99	0.7-3	3-5
Prismatic	3-15	1.58	99	0.5-2	3-6
Orthorhombic(Aragonitic)	9-13	1.63	99	0.5-2	4-8

3.1 Nano PCC

Nano PCC is a super and very narrow particle size distribution precipitated calcium carbonate specially formulated as functional filler and extender in industries such as plastic, rubber, paper, food, etc.

The crystals are those which are less than 100 nanometers or 0.1 microns in size with the specific surface area in a range of 15-30 m^2/gr. advanced technology allows the synthesis of calcium carbonates in nanoparticles with a large surface area. Each particle is surface coated with a modifier such as fatty acid, organic coupling agents, to improve dispersion and compatibility with polymer matrix [6].

4. PCC Applications

Precipitated calcium carbonate (PCC) is a versatile material that can be used in many industries such as paper making, pharmaceutical, cosmetic, paint, plastic, sealant, toothpaste, and food mainly as a filler product, Table 3, [1, 7].

Table 3: PCC global consumption rates [1]

Industry	Consumption %
Paper	72.0
Paints	8.0
Plastics	5.0
Rubber	4.5
Food, cosmetics, and pharmaceuticals	4.0
Textile packing	2.5
Putties, caulks, sealants	2.5
Adhesives	1.0

4.1. Paper & pulp

Calcium carbonate ($CaCO_3$) is used in large amounts in the pulp and paper industry as paper filler and in coatings to provide opacity, paper bulk, light scattering, improves paper machine productivity, and can reduce papermaking costs through the replacement of more expensive pulp fiber and optical brightening agents, and improved printability due to its good ink receptivity. In Finland, 700 kt/a of calcium carbonate is used for coating and 300 kt/an as a filler [8].

4.2 Plastic industries

Plastics are highly demanded in almost every industry. They show good mechanical properties when combined with polymers and polymer composites.

Precipitated calcium carbonate is used in various types of plastics as a highly effective impact modifier, rheology control agent and filler. Because it is chemically produced under strict process control, all aspects of the particle size distribution and particle morphology are controlled to exacting specifications.

The most important application of PCC in the plastic industry is in polyvinylchloride (PVC). The arguments favoring the use of precipitated calcium carbonate (PCC) as functional filler include low abrasiveness, improving the strength properties, higher whiteness and surface gloss, and better weather stability of the PVC window profiles [9, 10].

4.3. Paint &ink

PCC is used as a substitution for TiO_2 since its contribution to opacity is higher than the other filler substitutes. PCC production is a process of recrystallization of calcite under well-controlled conditions; hence, the products are purer than the other minerals. Due to this purity, paints containing PCC yield higher brightness than the standard paints which contain GCC as a pigment. PCC also increases the resistance of paint films against scrubbing and by preserving the color quality, there is a drop in final product cost. Precipitated calcium carbonate particles play a key role as a pigment in paints and all products in which used titanium dioxide [11, 12].

4.4. Pharmaceutical industries

Medical applications of $CaCO_3$ in modern health care systems have attracted the attention of researches due to its great potentials and capabilities.

Many medicines contain PCC, as the base material of pills, or for bulking of liquid medicines, ointments or creams. This material is low cost, safe and accessible. Furthermore, due to the slow Degradation and pH-sensitive properties, this material can be used as controlled release systems to maintain the drugs in targeted sites for extended times after administration [13].

4.5. Rubber industry

PCC already has a long history of using a rubber. Its use can reduce costs and can improve heat resistance, the stability of size and hardness of base materials. Calcium carbonate is a filler used for the first time by the rubber industry and is still used at the highest level. Adding calcium carbonate to rubber increases tensile strength, abrasion resistance, and tear resistance even more than does vulcanization. It can increase the volume of the products, which keeps the use of expensive natural rubber and thus reduces costs. Also, it has a significant role in reinforcing the natural rubber and synthetic rubber and can adjust the consistency [14].

4.6. Food industry

PCCs are a calcium source when added to fish and animal feed. It is also used by the food industry as a fortifying food and can be used as an additive in beverages. With high purity levels and stability, their small particle size and controlled particle shape offer good dispersion, suspension consistency, and mouthfeel. They can be used in a huge variety of food types such as Baked Goods, Bars, Beverages, Breakfast Cereals, Chewing Gum, Chocolates, Coffee Lighteners, Frozen Desserts, etc.

4.7. Cosmetic industry

PCC is used as filler in many cosmetic products and as an absorbent for perspiration and excess skin oil in powder form. Cosmetic products containing PCC include eye shadow, body powders, face powder, foundations, and make-up bases.

5. Marketing

Calcium carbonate is one of the widely used industrial fillers in various end-use industries.

According to a new market report published by Lucintel, the future of the calcium carbonate industry looks good with opportunities in the paper and plastic application segments. The calcium carbonate market is forecast to grow at a CAGR of 5.7% by value from 2015 to 2020. The global calcium carbonate market size is expected to be valued at USD 34.28 billion by 2025.

The major growth driver for this market is increasing paper demand from the packaging and printing market.

In this market, precipitated calcium carbonate (PCC) is used as a filler in paper, plastic, coating, rubber, adhesive, and sealant. Based on its comprehensive research, Lucintel forecasts that PCC will witness the highest growth during the forecast period, supported by increasing penetration and its attractive properties of high brightness, purity, and absorption level.

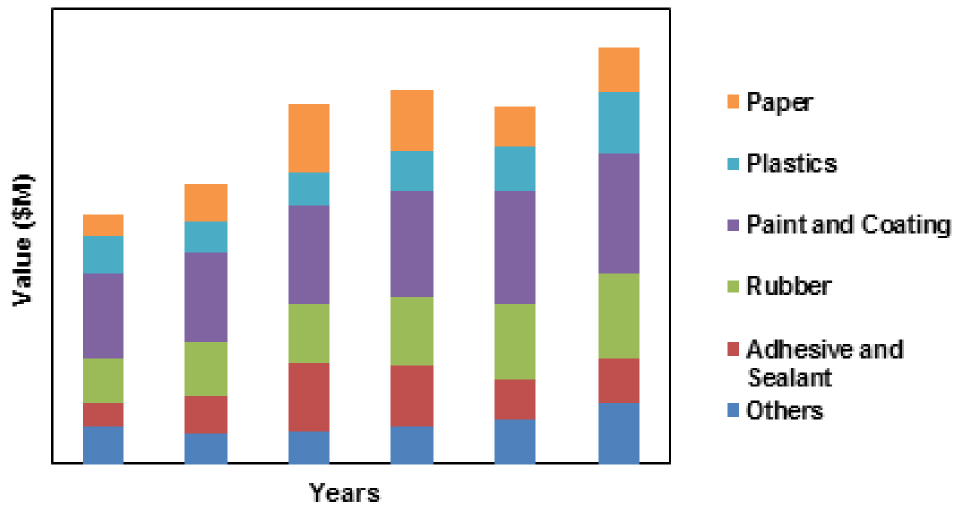
PCC is widely used in the paper mill as a filler material in the alkaline papermaking process. Growing demand for brighter and bulkier paper is the key driver behind the preference of calcium carbonate in the paper industry.

In the paper industry, PCC is valued worldwide for its high brightness and light scattering characteristics, and it is used as an inexpensive filler to make bright opaque paper. The filler is used at the wet-end of papermaking machines, and calcium carbonate filler makes the paper bright and smooth.

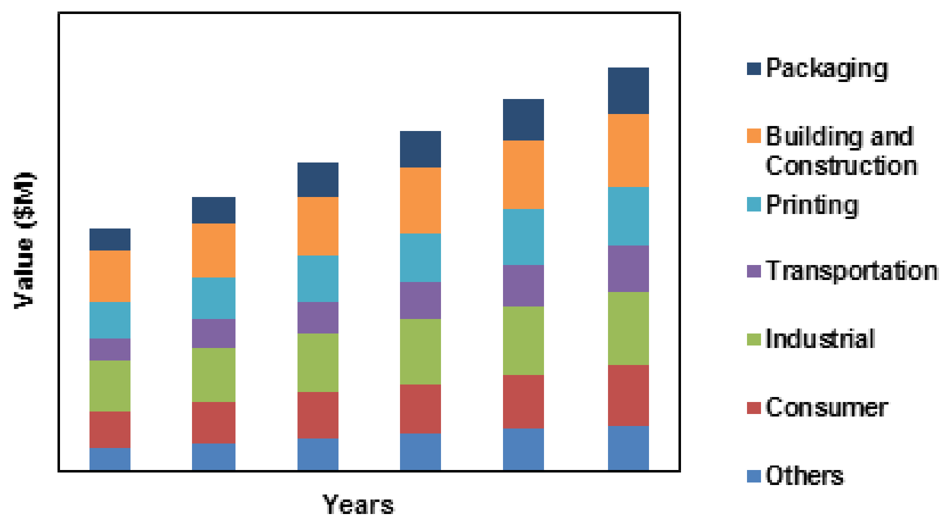
Both types of calcium carbonate, i.e., ground calcium carbonate (GCC) and precipitated calcium carbonate (PCC), are used in the paper industry. GCC filler material is used in an alkaline wood-free papermaking process. The brightness of GCC is 86%-95%. However, PCC is preferred over GCC in paper mills, since it provides better gloss and opacity properties for the paper, and the brightness of PCC is 90%-97%. PCC is the most cost-effective mineral for producing high-quality paper and paperboard via substitution of more expensive wood pulp, additives, or other minerals.

Based on geography, Asia Pacific is expected to remain the largest market due to the higher production of paper and plastics in China and India. North America and Europe are expected to witness good growth over the forecast period due to growth in the paper, plastic, and coating demand.

Overall, with the demand increasing from various end-user industries in the region, the market for calcium carbonate is projected to increase at a high rate during the forecast period [15, 16].



Global GCC and PCC Market trends by Application from 2011 to 2016



Global GCC and PCC Market forecast by end-use industry from 2011 to 2016

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