CALCIUM CARBONATE

1. Introduction

Calcium carbonate [471-34-1], $CaCO_3$, mol wt 100.09, occurs naturally as the principal constituent of limestone, marble, and chalk. Powdered calcium carbonate is produced by two methods on the industrial scale. It is quarried and ground from naturally occurring deposits and in some cases beneficiated. It is also made by precipitation from dissolved calcium hydroxide and carbon dioxide. The natural ground calcium carbonate and the precipitated material compete industrially based primarily on particle size and the characteristics imparted to a product.

Natural ground calcium carbonate has been used for years as the primary constituent of putty. Since 1945, the processing of natural calcium carbonate has seen the introduction of beneficiation by flotation (qv) to remove impurities and the development of grinding processes to manufacture finer products. Precipitated calcium carbonate was first introduced in England in 1850; commercial production started in the United States in about 1913.

Calcium carbonate is one of the most versatile mineral fillers (qv) and is consumed in a wide range of products including paper (qv), paint (qv), plastics, rubber, textiles (qv), caulks, sealants (qv), and printing inks (qv). High purity grades of both natural and precipitated calcium carbonate meet the requirements of the *Food Chemicals Codex* and the *United States Pharmacopeia* and are used in dentifrices (qv), cosmetics (qv), foods, and pharmaceuticals (qv).

2. Properties

Calcium carbonate occurs naturally in three crystal structures: calcite [13397-26-7], aragonite [14791-73-2], and, although rarely, vaterite. Calcite is

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Table 1. **Properties of Calcium Carbonate**

Property[a]	Calcite	Aragonite
specific gravity	2.60–2.75	2.92–2.94
hardness, Mohs'	3.0	3.5–4.0
solubility at 18°C, g/100 g H_2O	0.0013	0.0019
melting point, °C	1339[b] dec 900	[c]
index of refraction[d]		
α		1.530
β		1.680
γ		1.685
ω	1.658	
ε	1.486	

[a] Ref. 3.

[b] At 10.38 MPa (102.5 atm).

[c] Decomposes to calcite at temperatures >400°C.

[d] Ref. 2.

thermodynamically stable, aragonite is metastable and irreversibly changes to calcite when heated in dry air to about 400°C. Vaterite is metastable to calcite and aragonite under geological conditions but is found during the high temperature precipitation of calcium carbonate (1). The crystal forms of calcite are in the hexagonal system with $\bar{3}2/m$ symmetry; the crystals are varied in habit and over 300 different forms have been described. Aragonite is orthorhombic with 2/m2/m2/m symmetry and three crystal habits are common: acicular pyramidal, tabular, and pseudohexagonal (2).

The commercial grades of calcium carbonate from natural sources are either calcite, aragonite, or sedimentary chalk. In most precipitated grades aragonite is the predominant crystal structure. The essential properties of the two common crystal structures are shown in Table 1.

3. Manufacturing and Processing

3.1. Natural Calcium Carbonate. The production of natural ground calcium carbonate starts with the quarrying of a deposit of chalk, limestone, or marble. The best deposits for most industrial applications are those having a high (>90% $CaCO_3$) purity and high brightness. Most calcium carbonate quarries are of the open-pit type but there are underground operations. The ore is taken to a primary crusher for size reduction and then into the processing plant. The plant process is dependent on the grade of material being made. Typically, coarse products that do not require high purity, 90–98% $CaCO_3$, go to secondary crushing. This may be a cone- or jaw-type crusher that produces material minus 4 cm. Final grinding for products down to approximately 5 μm median particle size can be done in a roller mill or ball mill. Products finer than 10 μm often involve additional processing, usually in a dry ball mill circuit with air classification.

For those grades requiring high purity or finer material the process is different. Ideally, the secondary crushing step should reduce the ore to the point where mineral impurities are liberated, typically $<100\,\mu m$, without producing an excess of fines. The material may then be beneficiated through a mineral flotation process in which impurities are floated out. The flotation process produces a higher brightness material that is typically $>98\%$ calcium carbonate. Commonly, the flotation product is further ground in a ball mill to produce a product in the 2–50 μm particle range. Products having a median particle size less than 2 μm are usually wet ground in media or sand mills, the final product being a slurry that can be shipped after stabilizers and biocides are added, or dried for powdered products.

3.2. Precipitated Calcium Carbonate.

Precipitated calcium carbonate can be produced by several methods but only the carbonation process is commercially used in the United States. Limestone is calcined in a kiln to obtain carbon dioxide and quicklime. The quicklime is mixed with water to produce a milk-of-lime. Dry hydrated lime can also be used as a feedstock. Carbon dioxide gas is bubbled through the milk-of-lime in a reactor known as a carbonator. Gassing continues until the calcium hydroxide has been converted to the carbonate. The end point can be monitored chemically or by pH measurements. Reaction conditions determine the type of crystal, the size of particles, and the size distribution produced.

The reactions in this method are

calcination $CaCO_3 \rightarrow CaO + CO_2$

hydration or slaking $CaO + H_2O \rightarrow Ca(OH)_2$

carbonation $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

Following carbonation, the product can be further purified by screening. This screening, also used to control the maximum size of the product, is followed by dewatering (qv). Rotary vacuum filters, pressure filters, or centrifuges are used in the mechanical removal of water. Final drying is accomplished as with natural calcium carbonate in either a rotary, spray, or flash dryer. Products having mean particle sizes from submicrometers ($\sim$0.03 μm) to several micrometers are available.

New processes for preparing calcium carbonate with useful properties as paper filters have been described (4,5).

Both natural ground or precipitated calcium carbonate are available as dry products shipped in 22.7 kg multiwall bags, supersacks, or in bulk via truck and railcar. Calcium carbonate slurry, primarily used by the paper industry, is shipped by truck and rail. The solids content of these slurries is typically $>70\%$ by weight for ground products and 20–50% for precipitated. In the 1980s small precipitation plants were built at the site of large North American papermills.

Some grades of calcium carbonate are surface coated to improve handling properties and dispersability in plastics. Treatments used are fatty acids, resins, and wetting agents. Coating reduces the surface energy, thereby facilitating dispersion in organic binders.

4. Economic Aspects

Consumption of fine ground calcium carbonate is six times that of the precipitated calcium carbonate. In 1999, the global market for fine ground exceeded 18×10^6 tons and the market for precipitated calcium carbonate was 2.7×10^6 tons. The United States market for fine ground calcium carbonate is expected to grow at the rate of 2% through 2004. In Western Europe the consumption of fine ground $CaCO_3$ is used in the paper industry and exceeds the use of precipitated $CaCO_3$. In 1999, Japan consumed 2×10^6 t of fine ground, which was used mainly in the paper industry. Consumption in Japan grew at a rate of 4.3% between 1991 and 1999 and this trend was expected to continue (13).

5. Specifications, Standards, and Quality Control

The most comprehensive set of test methods for calcium carbonate has been assembled by the Pulverized Limestone Division of the National Stone Association. Methods for particle size, brightness, +325 mesh (44 μm), and percentage of calcium carbonate have been published; standards are available and have been well characterized (7). The Technical Association of the Pulp and Paper Industry (TAPPI) has published methods for calcium carbonate used in the paper industry (8).

Food and pharmaceutical grades of calcium carbonate are covered by the *Food Chemicals Codex* (9) and the *United States Pharmacopeia* (10) and subject to U.S. Food and Drug Administration Good Manufacturing Practices (11). Both purity requirements and test methods are available (9,10). Calcium carbonate is listed in the *U.S. Code of Federal Regulation* as a food additive, and is authorized for use in both paper and plastic food contact applications.

6. Health and Safety Factors

Calcium carbonate is listed as a food additive (9) and not considered a toxic material. The exposure to dust is regulated and a Threshold Limit Value–Time-Weighted Average (TLV–TWA) of 10 mg/m^3 is set (12). OSHA DEL for total dust is 15 mg/m^3 and for respirable fraction, it is 5 mg/m^3 (13). Both natural ground and precipitated calcium carbonates can contain low levels of impurities that are regulated. The impurities depend on the source of material, processing, and the final grade; impurities are typically trace metals and naturally occurring minerals.

7. Uses

The use of calcium carbonate in paint, paper, and plastics make up the principal part of the market. In the paper industry calcium carbonate products find two uses: as a filler in the papermaking process and as a part of the coating on paper.

The benefits of calcium carbonate in papermaking are brighter paper, greater resistance to yellowing and aging, and the economic advantage of substituting inexpensive calcium carbonate for expensive pulp (qv). Depending on paper grade and applications, calcium carbonate can be 25% or more of the sheet. Both ground natural and precipitated calcium carbonate are used as paper fillers depending on the application. Blends of ground and precipitated calcium carbonate have found use in an effort to optimize the properties of both products (see PAPERMAKING MATERIALS AND ADDITIVES) (14).

The other significant market for calcium carbonate in paper is as the pigment in paper coatings. Paper is coated to improve its brightness, opacity, printability, ink receptivity, and smoothness. Ultra fine (< 1 μm mean particle size) ground calcium carbonate, in addition to providing these properties, improves the rheology of coating formulations applied at coater speeds up to 1600 m/min. Calcium carbonate may be the sole pigment in the formulation or may be used in combination with other fillers (qv) such as kaolin (see CLAYS). In coating applications the use of ground natural calcium carbonate far exceeds that of precipitated material.

The plastics industry is a primary consumer of calcium carbonate products. Flexible and rigid PVC, polyolefins, thermosets, and elastomers (qv), including rubber, utilize a wide variety of coated and uncoated grades. Each of these plastics categories benefit by calcium carbonate's lower cost in relation to the polymer. In addition to cost savings, the use of calcium carbonate provides improvements in modulus, heat resistance, hardness, shrinkage reduction, and color fastness. Increases in impact strength and improvements in stability are also benefits, especially with the use of coated grades.

Increased loadings of calcium carbonate in thermosets reduce cost and provide better surface characteristics.

Calcium carbonate is one of the most common filler/extenders used in the paint and coatings industry. Consumer and contractor paint formulas can include products from submicrometer size to coarse mesh sizes. The main function of calcium carbonate in paint is as a low cost extender. It is also used to improve brightness, application properties, stability, and exposure resistance. Coarse products help to lower gloss and sheen or even provide textured finishes. The selection of product type and particle size is determined by the desired performance and cost of the coating.

Calcium carbonate is also used in industrial finishes and powder coatings. These paints typically include finer products; the primary purpose is rheological and gloss control. Calcium carbonate is also used in paints to extend and enhance the use of titanium dioxide. This is accomplished by using the finest of natural ground products or precipitated grades.

Calcium carbonate continues to be used in its original application, putty, as well as caulks, sealants (qv), adhesives (qv), and printing inks (qv). Large volumes are used in carpet backing and in joint cements. It is used to improve body, reinforcement, and other properties.

Calcium carbonate is used in flue gas desulfurization. This application by a variety of engineering processes traps the sulfur–oxygen compounds produced in the combustion of coal (qv) (see COAL CONVERSION PROCESS; EXHAUST CONTROL, INDUSTRIAL; SULFUR REMOVAL AND RECOVERY).

Calcium carbonate is used in food and pharmaceutical applications for both its chemical and physical properties. It is used as an antacid, as a calcium supplement in foods, as a mild abrasive in toothpaste, and in chewing gum to name only a few (see FOOD ADDITIVES). Calcium carbonate can be used as builder in detergent compositions (15).

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