LOCAL CALCIUM CARBONATE POWDER: ITS PROPERTIES AND APPLICATION AS FILLERS

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ABSTRACT

Calcium carbonate powder used as filler is produced from limestone. It is extremely difficult to define the limits of this mineral category. Its definition depends more on its uses than on its physical or chemical properties. Calcium carbonate filler comes in two forms: ground and light. Ground calcium carbonate is a low-quality product and is much cheaper than light calcium carbonate. It has been widely used in several industries. For several purposes, calcium carbonate filler must have high brightness and vary in size from a nominal 325 mesh to submicron material. For plastics and paint industry, they must have low oil absorption and ease of dispersion. Quantitative analysis of the market is difficult to compile due to lack of statistics in the field. However, the polymer and paint industry are the largest consumer of white carbonate filler. Calcium carbonate is essentially a fairly cheap product, despite the fact that sophisticated techniques are used in its production.

INTRODUCTION

Calcium carbonate produced from limestone is used in a wide range of industries. It is used as filler, iron and steel fluxes, lubricant or purifying agent in the manufacture of diverse industrial as well as consumer products. Among the main users of calcium carbonate powder as fillers or extenders in Malaysia are manufactures of rubber products, paints, plastics products and printing inks.

Limestone, the backbone of the calcium carbonate industry, exists in abundant quantities in the form of large mineral deposits found in Kuala Lumpur, Selangor, Perak and Perlis. The existence of a huge deposit of limestone around Ipoh has made Perak the major producer of calcium carbonate powder in Malaysia.

This article will be focused on the properties, its applications in various industries and the Malaysian market for white carbonate filler/extender products.
Terminology

The term "white carbonate fillers" that will be discussed in this article refers to ground limestone, marble, dolomite of chalk along with synthetically produced light calcium carbonate. Ground calcium carbonate (GCC) is produced by grinding limestone into very fine particles. Depending on its uses, fineness of the particles can range from mesh 325 (coarse) to mesh 1,000 (extremely fine). Grounded calcium carbonate of mesh 800 and above is classified as high grade. Light calcium carbonate (LCC), on the other hand, is produced by burning limestone to its diassociation temperature and reconstituting the components by controlled precipitation. If precipitation is done in the presence of a coating agent, activated calcium carbonate (ACC) is produced. Both the uncoated (referred to as precipitated calcium carbonate or PCC) and coated (ACC) forms are designated as light calcium carbonate (LCC) which are of much higher quality than the grounded form or GCC.

PROPERTIES

The properties required of filler/extender products have been described extensively elsewhere and it is only intended to give a brief review here to help explain the differences between the different types of carbonate product. The key functional properties are as follows: particle size and shape, brightness, absorption characteristics (of oil or polymer), dispersion characteristics, refractive index, and specific gravity. Although refractive index and specific gravity are virtually the same for the whole range of carbonate products, there is a remarkable degree of variation among the first three properties which gives rise to the wide diversity of carbonate grade available.

(i) Particle size and shape

There are many methods of determining particle size and particle-size distribution, but the most accurate is based on the Stokes principle. Particle size is important because brightness, viscosity and other physical properties are closely related to fineness. For example, in the polymer manufacture, the finer the particle size of a calcium carbonate filler the greater its reinforcing properties. Typical particle-size analyses of filler grades are shown in figure 1.

Although limestone, marble and chalk are all varieties of the mineral calcite, there are distinct physical differences between them. Limestone, marble and dolomite are generally crystalline rocks, whose particles and grinding display the characteristic rhombohedral structure of compact but pointed particles. Hence chalk whitening are generally softer, the individual particles are rounded and can be prepared more easily to wide range of particle sizes than other carbonates.
(ii) Brightness

Brightness (or whiteness), measured according to the Commission Internationale d'Eclairage (CIE) standards, varies widely in the various types of carbonate filler available. Generally the finer the mineral powders the whiter it becomes. Most fillers become more acceptable as they become whiter. Naturally for most applications the higher brightness commands a price premium. Chalk whittings have a whiteness index in the 83-93 range. White calcites and dolomites can have a whiteness as high as 96. Precipitated calcium carbonates whiteness is in the 96-100 range.

(iii) Oil absorption and dispersion

Low oil absorption is an important property for paint and plastic application. Basically the less oil or polymer absorbed by the filler or extender, the greater the quantity of active materials available for actually binding the compound. As a group, the calcium carbonate fillers have the lowest oil absorption of all the main bulk fillers. Within the group the compact crystalline calcites tend to have lower oil absorption than the more porous chalk. However, chalk chalk can be surface treated by coating the particles with fatty, or aliphatic acids. This treatment not only lowers oil absorption considerably but also gives significant improvements to the dispersion characteristics in plastic and rubber.

APPLICATION

Polymer user industries

Traditionally the particular merits of calcium carbonate were their ready availability, ease of dispersion and low cost - since they could not be used as reinforcing fillers as, for example, carbon black and precipitated silica. Recent developments both in polymers and in the technology of calcium carbonate production have, however, significantly altered this traditional pattern usage. In the most general terms, the finer the particle size of a calcium carbonate filler, the greater its reinforcing properties; and there are grades available today as ultrafine natural carbonates (which are much cheaper than PCC) which fulfil the particle size requirements of a semi-reinforcing filler.

In rubber manufacture, it is important to stress that although calcium carbonates cannot be used as true reinforcing fillers, they do not necessarily lower the strength of the product either. When ultra-fine carbonates is used in rubbers for extrusion or moulding, hot tear strength and elongation can be improved - and for extrusion purposes carbonates also has excellent dispersion characteristics. In Malaysia, ground calcium carbonate (GCC) is widely used in the rubber products industry as filler. The use of LCC, however, is restricted to the manufacture of inner tubes of tyres and footwear products.
With other polymers, notably PVC, polyester and epoxy resins, fine carbonate powder can be used to impart specific properties of mechanical, chemical or electrical resistance, and to inhibit shrinkage in extrusion and lamination applications. Ground calcium carbonate is used as filler in the manufacture of polyvinyl chloride (PVC) resins and compounds while precipitated LCC is used as lubricant only in PVC compounds in Malaysia.

Paint industry

White carbonates are probably the best all-round fillers for use in paints; they are used throughout the range of water, oil, plastics and latex paints for both interior and exterior purposes. Apart from lowering cost, ready availability and ease of dispersion, carbonate fillers can add brightness and hiding power, and impart good weather resistance.

Paint formulations are not expected to change radically in the near future as there is very little in the way of major technological change that will affect calcium carbonate consumption. There has been a greater amount of ultra-fine grades use in the paint recently as a replacement for greater amounts of titanium dioxide.

Calcium carbonate which is used locally in the paint industry (i.e. for emulsion and distempers and water-base paints) consists of the ground type (GCC) of 325 mesh up to 1,000 mesh. Water-based paints intended for undercoating utilize GCC of mesh 325 to 600. Higher quality water-based paints and emulsions require GCC of mesh 800 to 1,000. Premium grade emulsion paints do use light type (LCC).

Paper industry

Until the early nineteen-fifties, calcium carbonate could not be used as paper fillers because of the acidic conditions of rosin/alum sizing systems. However, since the development of neutral/alkaline systems, which began during that time, calcium carbonate has become a highly acceptable filler. Shorter size curing times, better retention of size and filler in the sheet, better machine running characteristics and improved surface qualities in the finished product have eliminated many of the shortcomings of neutral and alkaline sizing. The result has been a considerable increase in demand for good quality, low cost calcium carbonate fillers for printing and writing papers in Europe and North America. Calcium carbonate is also compatible with most optical whitening agents, which makes it an ideal filler for optically whitened cartridge papers.
Miscellaneous industrial purposes

The number of uses for calcium carbonates in industries other than those of polymer, paint and paper manufacture is very large. Industrial uses of calcium carbonate powder include the production of printing ink, linoleum, insecticide/herbicide/fungicide carriers, animal and human feedstuffs, mild abrasives (polishes, cream cleansers, etc.), ceramic, adhesives, road line paints, sports field paints, pharmaceutical and toiletry products, toothpaste formulation, dry wall joint cement, asphalt filler, etc.

MARKET AND PRICE

Total production of crushed carbonate rocks in Malaysia in 1986 was about 10.9 million tonnes according to the Geological Survey Malaysia. The proportion of this that is sold by producers as calcium carbonate powder amounted to 110,000 tonnes. The Department of Statistics lump up figures shows that Malaysia imports 10,451 tonnes of carbonates and percarbonates in 1986. The usage of carbonate powder varies considerably from industry to industry. Industries such as floor tiles or carpet backing require relatively coarse ground material, while asphalt filler is perfectly adequate for off white material. All of this makes it very difficult to compile accurate statistics for white carbonate filler market. However, the polymer industry (including rubber and plastic) is believed to be the largest consumer of white carbonate filler in Malaysia followed by the paint industry.

Information of the prices of calcium carbonate fillers are relatively easy to obtain but prices that reflect the market meaningfully are not. In Malaysia, there is considerable price competition over a wide range of grades. There are also so many different grades dependent on colour, particle size, particle size distribution, and coating, which makes it impossible to give an accurate indication of price. Calcium carbonate can sell for $50 - $850 per ton from the low end off white, relatively coarse material to a coated precipitated calcium carbonate (ACC).

CONCLUSION

Overall, the outlook for calcium carbonate fillers is promising. Current increasing demand for the production of rubber products such as gloves will increase the use of calcium carbonate fillers. With the expansion of the automobil industry in the near future in Malaysia, the demand for calcium carbonate fillers in the plastic industry (eg. for the manufacture of body panels in cars, etc.) is expected to increase rapidly soon.
Although many local manufactures have been involved in the making of calcium carbonate powder, the output is not fine enough to be used as filler for top quality products. It is desirable that local technology should be upgraded to improve the quality of the product so that local production could satisfy the demand for high grade calcium carbonate powder in Malaysia.

References


Fig. 1: Typical Particle-size Distribution of High Quality Filler Grades

% finer than

Equivalent spherical diameter - microns