

Chapter 9

Extender Particles



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Introduction

Extenders can be defined as colorless, or nearly colorless, particles with refractive indices below 1.7—that is, so low that the particles do not scatter light meaningfully when embedded in a polymer matrix [1–3]. These materials were introduced to the paints and plastics industries as simple fillers to replace resin or polymer with a less expensive substitute. While many extenders are still used in this passive manner, others take on a more active role, providing a means for the formulator to adjust and improve the performance attributes of their product [4–8].

The evolving importance of extenders can be attributed to two factors. First, paints and plastics have become more sophisticated over time, and as such, every opportunity is taken by the formulator to enhance product performance. Extenders offer

one such opportunity. Second, over the years the mining and extender manufacturing industries have undergone significant technological improvements, allowing for enhanced extenders to be produced economically. These enhancements apply to extender properties such as particle size, whiteness, and processibility in paint or plastics applications. The resulting particles are often referred to as “functional fillers”, highlighting the active part that these materials can play in polymer matrices. In this chapter and throughout this book, we will refer to these materials as “extenders” rather than “fillers”, as the latter term does not accurately convey the value that these particles bring to the paint and plastics industries.

Extender production is linked intimately to the mining industry. With few exceptions, the raw materials for extenders are minerals that are mined out of the ground. In some cases, these are simply cleaned and sold in essentially the same condition as they came out of the ground, while in other cases, they are processed more extensively. This processing can include more rigorous purification, grinding, and particle size separation (classification). In some cases, the natural minerals are reacted chemically to provide an intermediate material that is then back-reacted to the original mineral. This allows for improved purity and greater control of particle size.

The extender business is typically organized at the regional level. This is because the cost of transporting extenders over distances of more than a few hundred kilometers would add significantly to their overall costs, and because the raw materials for extenders are well distributed geographically, making them locally available in most cases. This can be contrasted to the pigments business, which is typically global and can involve intercontinental transportation.

Important Extender Properties

Many paints and plastics’ properties can be affected by extender particles. Table 9.1 summarizes the most important of these properties [7, 9, 10]. Many of the effects that extenders have on the properties listed in this table are based on the physical properties of the extender particles themselves. Many of these effects are similar for extenders that share certain properties. For example, the effect that a certain size of platelet particles will have on paint rheology is similar for all platelet extenders of that size, regardless of their chemical or mineral composition. The extender’s physical properties that affect paint and plastic performance include, in rough order of importance, particle size (and size distribution), particle shape (and aspect ratio, for non-uniform particles), particle porosity, particle packing ability, and particle hardness. In addition, some chemical properties of extenders can affect paint and plastic performance. These are the pH of the particle surface, as well as the reactivity of the particle to water, acids, bases, salts, and solvents.

Particle size and size distribution are important for a number of reasons. In general, extenders cover the range of 0.01 to 45 microns, although most are in the range of 0.5 to 10 microns. This range is limited for practical reasons. The use of particles at the high end of the range can cause defects in paint or plastic films, while the use

Table 9.1 End-Use Properties of Paints and Plastics that can be Affected by Extender Particles

Paints	Plastics
• Flow and Viscosity	• Process aid
• Settling	• Shorter fusion time
• Strength/toughness	• Melt flow and extensibility
• Reinforcement	• Nucleation for crystallization
• Cracking and shrinking	• Moldability
• Scrub and abrasion resistance	• Strength
• Burnish	• Impact
• Adhesion (to substrate and inter coat)	• Modulus
• Gas and liquid permeability	• Stiffness
• Weather resistance	• Tensile
• Corrosion resistance	• Reinforcement
• Dry Hide	• Shrinkage/thermal expansion
• Gloss	• Gas and liquid permeability
	• Weather resistance

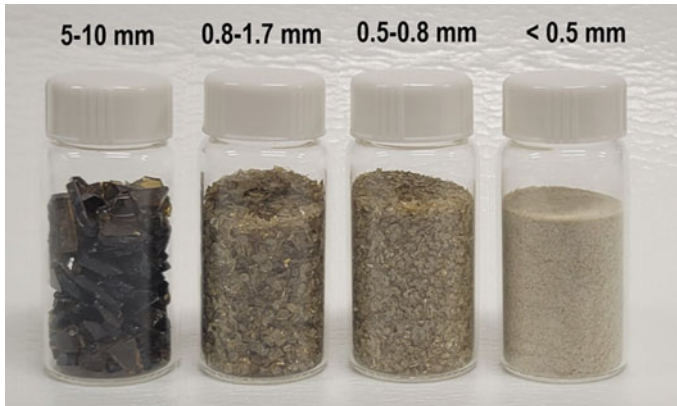
of particles at the low end of the range can cause excessively high viscosity in the liquid paint or polymer melt.

There are many times more particles in a gram of small size extender than there are in a gram of large size extender. For identically shaped particles, the number of particles decreases as the third power of particle size. Likewise, a gram of small particles has a greater surface area than a gram of large particles. In this case, the change is linear with particle size. Higher surface areas increase the amount of material that a unit weight of particles can adsorb, which increases oil absorption¹ and binder demand in paints. Higher surface areas also increase the magnitude of particle–particle attractions, since these occur at particle surfaces. This affects the dispersibility of the particles in both a liquid paint and a polymer melt.

Particle size can influence the color or brightness of an extender. In their pure form, the minerals used as extenders are colorless. However, there are invariably colored impurities present in those that are mined. These colored impurities can be reduced through purification, but it is difficult to entirely eliminate discoloration. However, since small particles scatter light more efficiently than an equal weight of large particles, as the particle size is reduced, the material becomes brighter and whiter.

This effect can be demonstrated using macroscopic glass particles. Figure 9.1a shows four particle sizes of the same brown glass (refractive index 1.52). As can be

¹ Oil absorption refers to the grams of linseed oil needed to “liquify” one hundred grams of particles (see Chapter 2).



(a)



(b)

Fig. 9.1 Brown glass particles of different sizes. **a** Particles in air. **b** Particles immersed in mineral oil. Adapted from [10]

seen, in air (refractive index 1.0), the smallest particles are merely off-white, while the largest particles are intensely colored. This brightening effect is significantly reduced when the particles are embedded in a resin or polymer matrix, since the higher refractive indices of these matrices (1.50–1.60) reduce the light scattering ability of the particles. This can be seen in Fig. 9.1b, where mineral oil (refractive index 1.49) has been added to the particles.

Particle size distribution is important because particles with a broad size distribution can pack more densely than those with a narrow distribution. This is because the smaller particles can pack into the voids between the larger ones (refer to Chaps. 4 and 16). Related to this, small extender particles (< one micron) are capable of situating themselves between pigmentary particles, which typically have sizes between 0.2

and 2.0 microns. These small extender particles improve the spacing of the pigmentary particles in comparison to the same volume of large extender particles, since the latter crowd the pigmentary particles into confined regions. Particle packing also affects the critical pigment volume concentration (CPVC) of paint, as discussed in Chap. 4, as well as the melt flow viscosity of plastics. There is still much detail to learn about the effects of particle size distribution on the properties of paints and plastics, and this is an area of active research [11, 12].

Particle shape affects a number of physical properties of the paint or plastic. As discussed in Chap. 1, particle shapes can be categorized into three groups, although the demarcation between these is often blurry. These categories are the acicular one-dimensional particles (needles, rods, and fibers); the plate-like two-dimensional particles (platelets); and the solid three-dimensional particles (nodules or blocks). As a general rule, when different particle shapes behave differently in an application, two-dimensional particles behave more similarly to one-dimensional particles than to three-dimensional particles.

Particle shape is often determined by the type and arrangement of atoms in the solid. In this regard, there are two basic types of extenders—insoluble salts and oxides. Both can be hydrated with water of crystallization. The most common salt extenders are calcium carbonate and barium sulfate. The structure of salts is such that discrete cations and anions alternate in all directions, leading to a three-dimensional, blocky particle.

The atomic arrangements in oxide extenders are more complex. In general, these consists of networks of metal cations (typically aluminum or silicon) bridged by oxygen or hydroxide anions. These networks can be one-dimensional chains, as in wollastonite, two-dimensional sheets, as in kaolin, talc, and mica, or three-dimensional space-filling structures, as in feldspar and silica. The bonds within networks are typically quite strong (ionic or covalent bonds), while the bonds between the networks are much weaker (hydrogen or van der Waals bonds). Particles generally extend the greatest in the direction of the strongest bonds, and so wollastonite particles are needles, kaolin, talc, and mica particles are platelets, and feldspar and silica particles are blocks.

Each particle shape confers certain properties to the material in which they are embedded. Perhaps the most important effect of needles is their ability to provide strength to a paint film or plastic object. When oriented randomly, they reinforce these materials in all three dimensions. This reinforcement is manifested in a number of ways, particularly in plastics, where several strength parameters can be affected (bending strength, impact resistance, stiffness, etc.). In paints, this can lead to impact resistance (which is important for automotive paints) as well as scratch resistance.

Needles also affect the viscosity of a liquid paint or a polymer melt through their formation into weak networks. In paints, these networks are designed to quickly form under conditions of no shear, such as during storage or immediately after application to a substrate, and to break down under the shearing action of paint application (by brush, roller or spray device). This allows the paint to be easily applied to the substrate yet also resist running or sagging after application. It also prevents sedimentation of

other particles in paints while they are stored, since these particles will be trapped in the network of needle-shaped particles.

Platelets also affect paint viscosity and polymer melt flow in the same ways. In addition, should settling of paints occur, the consistency of sediments that contain platelets is typically such that they can be easily reincorporated into the paint through simple stirring. When platelets are aligned and oriented parallel to a painted surface, they increase substrate protection by reducing the permeability of the paint to air, water vapor, liquid water, and corrosive chemicals. This reduced permeability is due to the tortuous path that an intruding molecule must travel to reach the substrate surface.

Both needles and platelets can decrease crack formation during the paint drying process. Paints will “mud crack” during drying if stresses due to film contraction exceed a certain threshold. This is a common concern for dilute paints, which lose much volume during drying, as well as for thickly applied paints, from which solvent or water often evaporates unevenly. This temporarily forms regions with different physical properties. Needles and platelets can relieve these stresses as they are created, preventing crack formation.

Platelets, like needles, reinforce plastics and increase many of their strength attributes. However, platelets tend to orient along melt flow lines, which results in strength improvements in only two directions, rather than in all three dimensions. In addition to this reinforcement effect, platelets and needles can improve strength by acting as concentration and relief points for stress.

Blocky particles have a lesser effect on the properties of paints and plastics because they do not form extensive networks. As such their effect on viscosity is minimal except at high concentrations. In addition, they do not reinforce paints and plastics in the same way as needles and platelets, although they can act as concentration points for stress. This allows for some level of strength improvement.

There are also several important effects of extenders that are not related to their size or shape. Hard particles improve the abrasion and scratch resistance of plastics and paint films, but also increase the abrasion of equipment during processing. Particles near a surface can roughen it, providing a means to control the sheen in paints and plastics. In addition, these particles can provide a “tooth” to a paint—that is, increase the adhesion between the paint and the substrate, and the inter-coat adhesion between layers of paint. When used at high concentrations in paints, extenders improve opacity through dry hide, which is light scattering by air voids within the paint (see Chaps. 4 and 7). Finally, low levels of some extenders can be used as anti-blocking agents in plastic films, preventing sheets of film from sticking to one another.

The surface character of extender particles plays an important role in both paint and plastic applications. It is important that the surface is compatible with its surrounding matrix. In paint films and plastics, this matrix is a polymer, while for liquid paints it is water or a solvent. Most extender particles are hydrates, which makes them hydrophilic and, as a general rule, easily dispersed and stabilized in water. Particle surfaces can be modified by the application of a hydrophobic material, such as a stearate or silane, leading to stronger binding of the polymer to the particle surface. This improves processibility in plastics [13] and corrosion protection in paints [14].

Table 9.2 Important Properties of Extenders

Mineral	Chemical Composition	Mohs Hardness	Density g/ml	Refractive index	Particle Shape
Calcium Carbonate	CaCO ₃	3	2.6–2.8	1.59	Nodular
Dolomite	Ca/Mg(CO ₃)	3.5–4	2.8–2.9	1.62	Nodular
Kaolinite	Al ₄ (OH) ₈ Si ₄ O ₁₀	1–2	2.6	1.56	Platelet
Calcined Kaolin	Al ₄ (OH) ₈ Si ₄ O ₁₀	5–6	2.6	1.62	Platelet
Talc	Mg ₃ (OH) ₂ (Si ₂ O ₅) ₂	1	2.6–2.8	1.57	Platelet
Mica (muscovite)	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	2.5	2.82	1.56	Platelet
Feldspar	KAlSi ₃ O ₈	6	2.5–2.6	1.53	Nodular
Wollastonite	CaSiO ₃	4.5–5.5	2.84	1.6	Acicular
Precipitated aluminum silicate	Various	–	2.1	1.46	Nodular
Quartz	SiO ₂	7	2.65	1.55	Nodular
Diatomaceous earth	SiO ₂	5.5	2.0–2.34	1.45	Complex
Barite	BaSO ₄	3.3	4.48	1.65	Nodular
Calcium sulfate	CaSO ₄	3.5	2.97	1.58	Nodular

Many of the effects of extender particles on paints and plastics properties are not linear with extender concentration. For example, properties that are strictly surface related, such as anti-blocking, respond rapidly to increases in extender concentration up to a point, that point being when the surface region is saturated with particles. Other properties vary with particle concentration in a more complex way. When testing or characterizing an extender in a paint or plastic, it is best to do so on a full series of particle concentrations, rather than to extrapolate from the results at only one or two concentrations.

For convenience, many of the most important physical properties of the extender types that will be discussed in this chapter are given in Table 9.2. Note that this list excludes some factors that are important in only limited applications, such as electrical impedance and magnetic characteristics.

Classification of Extenders

Given the wide variety of extenders used in the paint and plastics industry, it is useful to classify and organize these materials in some logical way. Since most commercial extenders originate from natural mineral deposits, the first level of classification can be made according to mineral origin. There are four broad classes of minerals used

as extenders: carbonates, silicates, different forms of silica, and others. In each case, there are several important sub-types. The majority of these are discussed below, starting with the carbonates.

The Carbonates

The term “carbonate” refers to any material that contains the CO_3^{2-} anion. There is a multitude of cations that can counter the charge of the carbonate ion, including Ca^{2+} , Mg^{2+} , Na^+ , K^+ , and H^+ . Of these, calcium carbonate and a mix of calcium and magnesium carbonate (dolomite) are the most commonly used extenders in the paint, plastics, and paper industries. This is due to their high brightness and commercial affordability. The high demand for these materials results in a broad choice of carbonate extender products [15].

Calcium carbonate, also known as calcite or limestone, forms under a number of geological conditions. Most calcium carbonate originates biogenically through the deposition of clam or other shells, although some are also formed by direct precipitation from fresh or ocean waters. When a carbonate sediment is formed, it is gradually compacted under its own weight, resulting in the formation of chalk. Chalk particles are typically a few microns in size, and even after grinding, the remains of seashells can be observed under the electron microscope.

Under increasing pressure from the overlaying of more sediment or other rock, the pores in chalk fill with precipitated calcite, forming limestone. When the temperature increases to between 200 and 500 °C and the pressure rises above 1000 bar, the limestone melts [2]. It then crystallizes slowly as marble, which is a metamorphic form of calcium carbonate. The purity of the calcium carbonate typically increases as a result of this crystallization. Because even small amounts of certain impurities (for example Fe^{2+}) can cause strong discoloration, the increased purity of marble gives it higher brightness and lower yellowness than chalk or limestone.

Calcium carbonate deposits are widespread, and each deposit has its own characteristic particle size, shape, and impurity profile. Because they originate as surface deposits, calcium carbonates are generally found close to the surface and so are relatively easy to mine. Both limestone and marble are used extensively to make calcium carbonate extenders. Chalk is less favored as an extender due to its higher concentration of colored impurities.

Calcium carbonate extenders process very well in both water-borne and solvent-borne coatings. Their surface areas are typically low, with values between 1 to 10 m^2/g , but can go up to as high as 20 m^2/g for the most finely ground natural particles as well as those formed synthetically by precipitation. As a consequence of their low surface area, the oil absorption and binder demand are both relatively low, with oil absorption values generally varying between 12 and 25 g oil per 100 g particles [2].

Due to their blocky shapes, calcium carbonate particles do not form extensive networks in slurries or liquid paints, and so they have only a moderate thickening effect on them. The lack of network formation allows for calcium carbonate levels

as high as 60% in paints, in contrast to many other extenders, such as talc and mica, that can only be used at much lower levels.

Calcium carbonate dissolves in acids, releasing CO_2 . Since most water-borne coatings are formulated under alkali conditions, this is seldom a problem. However, some paints, such as those that are used for cathodic electrodeposition, and wood coatings that are based on cationic resins, are formulated at pH values of 6.5 or less, and so cannot use calcium carbonate as an extender. Calcium carbonates are often used in anti-corrosion applications, where they buffer the coating at relatively high pH values.

Calcium carbonate can be used to improve paint opacity. There are two different ways that this can be accomplished. The first is to raise the volume concentration of particles in the dry film to a level above the critical pigment volume concentration, or CPVC. As was discussed in Chap. 4, this results in the incorporation of air voids into the film that, due to the low refractive index of air, provide light scattering and opacity.

Second, particles that are close in size to TiO_2 are claimed to act as spacers, separating the TiO_2 particles and thereby increasing their scattering efficiency. This is most often seen when larger extender particles, which tend to crowd the TiO_2 particles together, are replaced with smaller extender particles. In this case, the improvement in opacity is not due to active spacing on the part of the small extender, but instead to the reduction of active crowding on the part of the large extender [16].

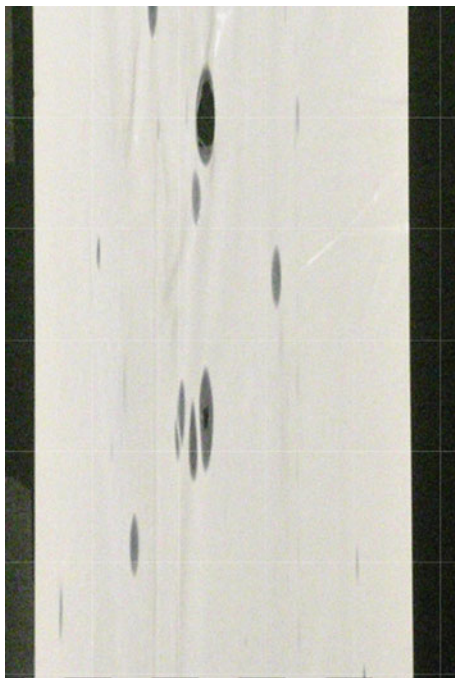
Calcium carbonate accounts for more than half of the total amount of extenders used by the plastics industry. Its extensive use can be attributed to many of the same factors that lead to its wide use in paints. In addition, calcium carbonate has no water of crystallization, which makes it ideally suitable for high-temperature plastics processing, where water volatilization can be problematic.² This is particularly true for plastic films. Here water vapor bubbles can form holes in the film, which are then enlarged as the film is pulled during processing (Fig. 9.2), creating severe defects in the film product. This process is known as lacing, since in the more extreme cases the resulting film strongly resembles lace fabric.

Calcium carbonate also reduces plastics shrinkage, has good anti-plate out properties, and can be conveniently surface treated with stearic acid (or a stearic acid salt) for improved processing. It does not strongly reinforce plastics in the same way as platelets or needles, although it does improve impact resistance. Thermoplastics are the largest single application for calcium carbonates in plastics, with lesser amounts used in elastomers and thermosets [17]. Of the carbonate types, ground calcium carbonate (see below) is used predominantly in plastic applications.

Calcium carbonate extenders are generally available in two forms that differ in manufacture, both of which can be further surface modified with fatty acids. The simpler form, ground calcium carbonate (GCC), is made by physically processing material that is directly extracted from the earth. Dolomite extenders, which are closely related to calcium carbonate extenders, are also processed in this way. The

² Other extenders lacking waters of crystallization are available, but these typically require the costly and energy consuming calcination of hydrated materials.

Fig. 9.2 Lacing of a polymer film due to water vaporization during processing



second form of calcium carbonate extender is precipitated calcium carbonate (PCC), which is manufactured by heating calcium carbonate to form lime (CaO), then reacting the lime with carbon dioxide to remake calcium carbonate (this is further detailed in the section below on the production of synthetic extenders). Purity and particle size can be more finely controlled by this process than by the GCC process.

We will discuss each of these materials in turns, beginning with GCC.

Ground Calcium Carbonates (GCC)

The ground calcium carbonate grades used as paint and plastics extenders typically have median particle diameters (D_{50})³ between 2 and 15 microns, although smaller particles ($D_{50} < 0.5$ microns) can also be made. Both wet grinding and dry grinding can be used to reduce particles. Fatty acids are often used to enhance grinding.

The wet grinding process allows for smaller and more uniformly sized particles but requires the additional steps of water separation (typically by filtration) and drying. In addition, wet grinding allows for colored impurities to be removed via flotation, and it is more cost-efficient than dry grinding when grinding to small particle size. This is partly because high electrostatic charges build up in the dry grinding

³ D_{50} is the diameter for which half the particles (by weight) are larger and half are smaller. See Chapter 2 for additional details on particle size determination.

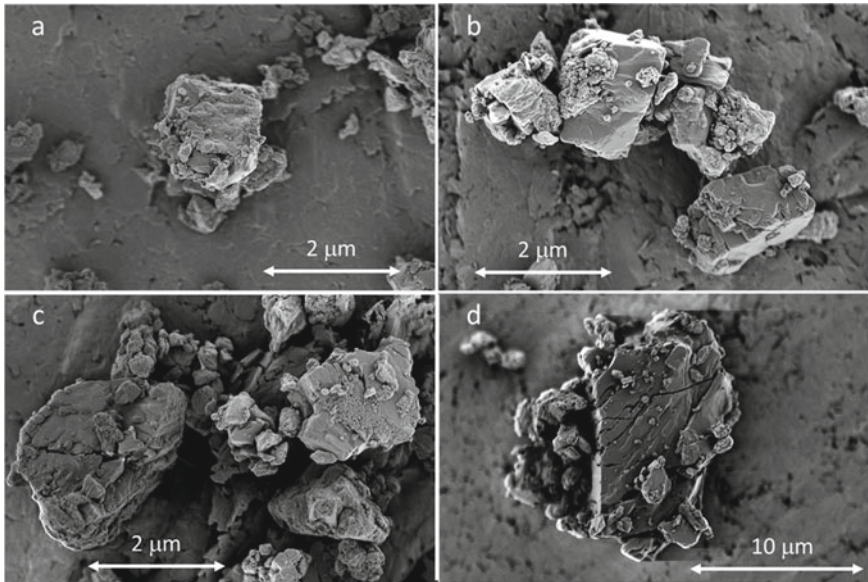


Fig. 9.3 Micrographs of ground CaCO_3 with different median particle diameters **a** wet ground CaCO_3 (D_{50} particle size 0.7 micron). **b–d** dry ground CaCO_3 with D_{50} particle sizes of 0.9 microns, 5 microns, and 15 microns, respectively (courtesy of E. Najafi and H. Huezo, Chemours)

process once the particles are reduced below a certain size. On the other side of the size spectrum, particle sizes up to several millimeters are used in putties, plasters, mineral adhesives, and sealants. Examples of typical GCC materials processed by these different grinding techniques are shown in Fig. 9.3.

Ground calcium carbonate is known for its blocky morphology, which distinguishes it from the more common platelet and needle structures of other extenders. As can be seen in Fig. 9.3, the distribution of particle sizes within a sample can be quite broad and can include particles with diameters as low as 0.2 microns, even in the largest average particle size sample. (Fig. 9.3d) Grinding decreases particle size not only by shifting the size distribution to smaller particles, but also by increasing the population of very small particles. That is, grinding not only alters the median particle size; but also alters the width of the particle size distribution [2].

In plastics applications, GCC materials are used both in their traditional capacity as extenders as well as to create opaque micro-voids in polypropylene and polyethylene films. To do this, small calcium carbonate particles (1 to 2 microns), often pretreated with a fatty acid such as stearic acid, are incorporated into these films, which are then stretched. These particles do not adhere strongly to the polymer, and when the films are stretched, the polymer pulls away from the particle surface. This creates elongated holes around the particles that, as described in Chap. 7, provide for opacity through light scattering.

Precipitated Calcium Carbonate (PCC)

While GCC is characterized by a nodular shape, precipitated calcium carbonates can have several different particle shapes depending on the manufacturing conditions. As shown in Fig. 9.4, PCC particle sizes can be much smaller than those of ground CaCO_3 . This is because small particle sizes are attained when the particles form, rather than through a grinding step. In addition to a lower overall particle size, the size distributions of PCC extenders are narrower than those of GCC extenders. PCC extenders are also brighter and less yellow than their GCC counterparts. These factors combine to give a very good overall performance of PCC extenders in paint and plastics applications. However, this good performance comes at a cost—the selling prices for PCC extenders are significantly higher than those of their GCC counterparts, due to the costs of the additional processing steps.

Historically, PCC extenders have been favored in plastics applications over their GCC counterparts because of their finer particle size—polymer grade PCCs are typically between 0.02 and 0.1 microns [17]. However, their higher cost has been an issue for use in these applications. Over time advances in GCC processing have improved the performance of these materials in plastics, though, resulting in a shift to GCC extenders in many applications.

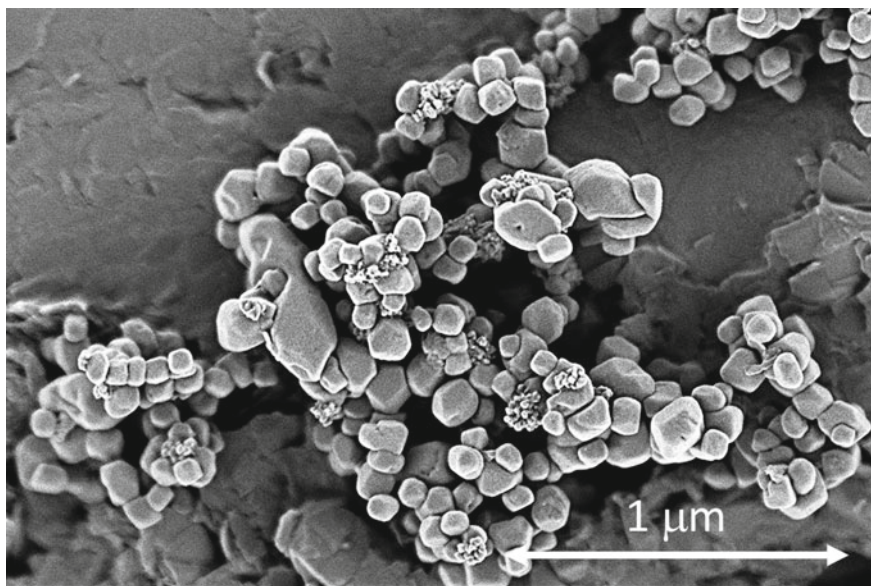


Fig. 9.4 Micrograph of precipitated CaCO_3 (courtesy of E. Najafi and H. Huezo, Chemours)

Dolomite

Dolomite is a mixed carbonate with roughly equimolar amounts of calcium and magnesium. Extenders made from dolomite are not as widespread as those based on calcium carbonate, due to their lower abundance and slightly higher cost. The properties of dolomite are generally in line with those of calcium carbonate, except it is slightly higher density, hardness, whiteness, and reactivity. The higher density of dolomite gives it a slightly higher bulk density and better flow than calcium carbonate. Like calcium carbonate, dolomite is hydrophilic and disperses quickly and easily in water. Also, like calcium carbonate, every deposit has its own set of unique properties. Overall, dolomites can be used in paints nearly interchangeably with GCC.

Silicates

Silicates are among the most diverse class of minerals. They are also quite widespread, making up over three quarters of the Earth's crust. Despite their large variety, all silicates have one structural feature in common—they all contain silicon atoms that are surrounded by a tetrahedron of four oxygen atoms. The various silicates differ in the ways that these tetrahedra are arranged, both with respect to one another and with respect to tetrahedra or octahedra formed by other atoms, most typically aluminum, magnesium, or alkali metals. The oxygen atoms are shared between these polyhedra, typically bridging two or three silicon or other metal atoms. In some cases, the oxygen atoms are bound to hydrogen atoms, forming hydroxyl groups that can bridge two or more metal atoms or can form hydrogen bonds to other oxygen atoms. Hydroxyl groups are also present at the particle surface.

A number of silicates are used as extenders in paints and plastics. We will discuss six of the most common, beginning with kaolin.

Kaolin

Kaolin, also called china clay or simply clay, is an important extender for coatings and, to a lesser extent, plastics. Kaolin is composed primarily of the mineral kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$), with lesser amounts of other minerals such as feldspar, quartz, and talc. It is produced in three forms—hydrous kaolin, partially dehydrated kaolin (metakaolin), and fully dehydrated (anhydrous) kaolin. The fully dehydrated kaolin can be made by two processes, each giving different properties. These processes are conventional calcination and flash calcination. The advantage of flash calcination is that it produces particles with sealed air voids. These voids increase the opacity in paints and plastics via light scattering. Representative electron micrographs of these various forms of kaolin are shown in Fig. 9.5.

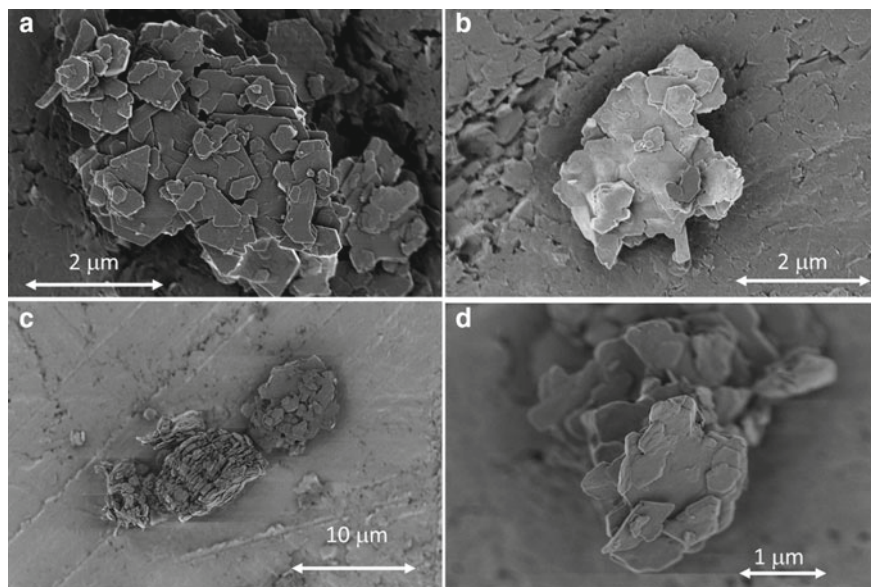


Fig. 9.5 Electron micrographs of kaolin extenders (courtesy of E. Najafi and H. Huezo, Chemours)

Kaolin deposits are distributed globally and are formed by the weathering of aluminosilicate minerals such as feldspar. Kaolin is typically found as a soft clay (2.5 on the Mohs scale) that can be extracted through either wet or dry mining. In its native state, it is usually discolored, but brightness can be increased to relatively high levels through purification and/or calcination. Calcination also increases particle hardness, bringing it to a value between 4 and 5 on the Mohs scale.

At the atomic level, kaolin can best be described as sheets of Si_2O_5 layers bound to sheets of $\text{Al}_2(\text{OH})_4$ layers (Fig. 9.6). The sheets are held together by hydrogen bonding, and as such crystals of kaolin are typically found as platelets with aspect ratios (width to height) between 5:1 and 20:1. The widths of materials used as extenders can be as high as 10 microns [18]. However, the widths of the particles used in paints and plastics are more typically between 0.2 and 5 microns. The smallest particles that are used as extenders can have aspect ratios as high as 50:1. Sheet-like silica arrangements such as those in kaolin are quite common in nature, and minerals containing them are termed phyllosilicates.

Calcination of hydrous kaolin results in an increase in particle size due to the bonding together of the faces of different particles [18, 20–22]. That said, small size calcined kaolin products are widely used—these are made by calcination of especially small hydrous kaolin particles. The merging together of particles during calcination gives these particles a blockier shape than the hydrated particles.

Kaolin is mostly used in paper applications, where it supplies brightness and opacity. However, the hydrated and anhydrous forms are also used extensively in paints, and the anhydrous form is sometimes used in plastics. Metakaolin, which is

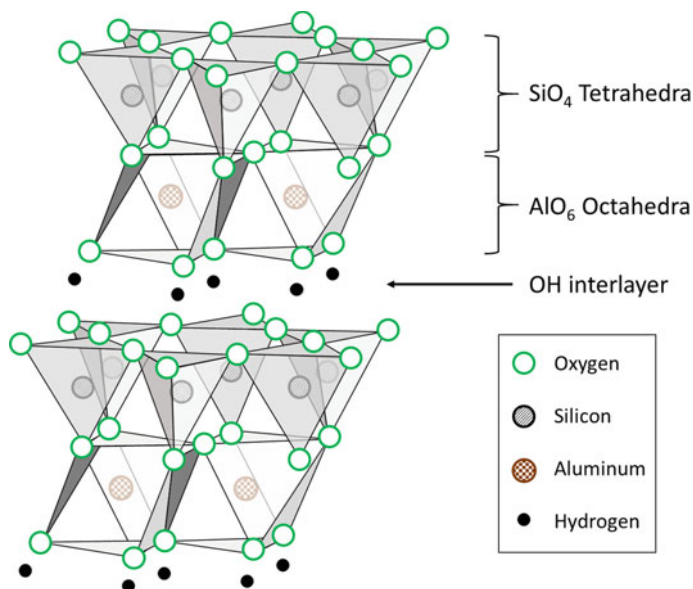


Fig. 9.6 Atomic structure of kaolinite. Adapted from [19]

incompletely dehydrated kaolin, is used in cement but seldom found in paints. It can be used in PVC cable [18] and has been investigated as an extender for thermoplastics [23].

Kaolin is hydrophilic and so disperses easily in water. Its platy structure affects the rheology of liquid paints, giving them body and improving flow properties such as improved brushability, sag resistance, and leveling. They also minimize crack formation during drying and sedimentation during storage.

Due to the platy nature of these particles, they reinforce dry paint films, increasing their toughness and burnish resistance (burnish is an increase in gloss when dry paints are rubbed). They also improve film adhesion to the substrate and to any overcoats of paint. Kaolin improves the weatherability of paints by reducing water permeability, and for this reason, it is sometimes found in highly durable industrial paints.

Under conditions of very low shear (for example, during storage, when gravity is the only shear force), the faces and edges of kaolin platelets interact, organizing the particles into a “house of cards” structure (Fig. 9.7a). This occurs because the edges of the particles are silica rich, and thus negatively charged, while the faces are alumina rich, and thus positively charged. This structure can be easily broken down in paints by stirring or by application using a brush or roller, both of which generate shear. Under shear conditions, the platelets align in a different fashion (Fig. 9.7b). The organized structure quickly reforms after paint application, preventing the paint from dripping or sagging. The structure can also be either further stabilized or destabilized by the addition of ions that can alter the charge on the particle edges [18].

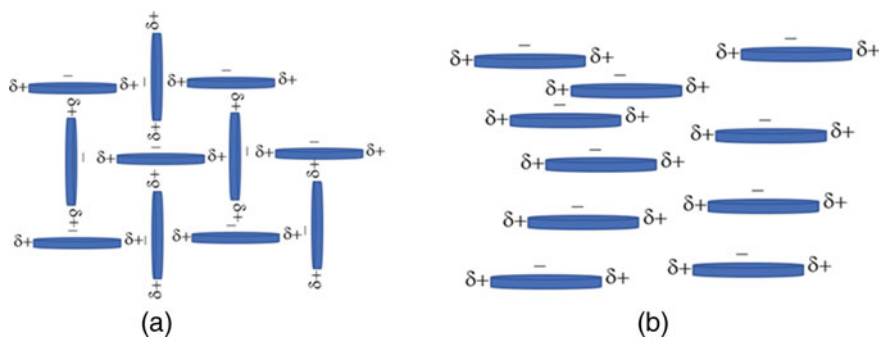


Fig. 9.7 Schematic representation of the self-organizing structures of clays at **a** low shear and at **b** high shear [24]

Hydrous grades, due to their small size, can be used in high gloss paints. They are commonly used in paints formulated below the CPVC, where they are claimed to improve the spacing between TiO_2 particles, allowing for some reduction of TiO_2 without a loss in opacity. Calcined grades are used in paints above the CPVC, where they increase opacity through dry hide (see Chap. 4). While they are considered to be more efficient at providing dry hide than hydrous kaolin or calcium carbonate, their larger size relegates them to matt or flat finishes. Brightness and opacity improvements are the main factors dictating the choice of kaolin above other extenders.

Kaolin is less prevalent in plastic applications due to its water of crystallization, relatively poor color, and poor heat aging in use. Calcined grades are more commonly used than hydrous grades, and these materials are often surface modified with stearic acid or silanes for better dispersibility and compatibility with the polymer matrix [18]. The finest grades (<2 microns) improve the tensile strength of plastics. They are used at low levels as anti-blocking agents for plastic films.

Talc

Talc (or talcum) is a common mineral with the chemical formula $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. It is perhaps best known for its softness and is, in fact, the softest mineral, with a defined Mohs value of 1. This limits scratch and scrub resistance in paints and plastics, and it also lessens the wear of production equipment and minimizes discoloration due to this wear. It is formed when calcium is washed from other minerals by carbonated groundwater. As is true of most mined extenders, many properties, such as degree of discoloration, particle size, and impurity profile, will vary depending on the source.

The atomic structure of talc consists of oxide sheets stacked on top of one another [25]. These sheets, in turn, are composed of a two-dimensional layer of octahedral $\text{MgO}_4(\text{OH})_2$ sandwiched between a pair of two-dimensional layers of tetrahedral SiO_4 (Fig. 9.8). The structure of these sheets is common in mineralogy, and they

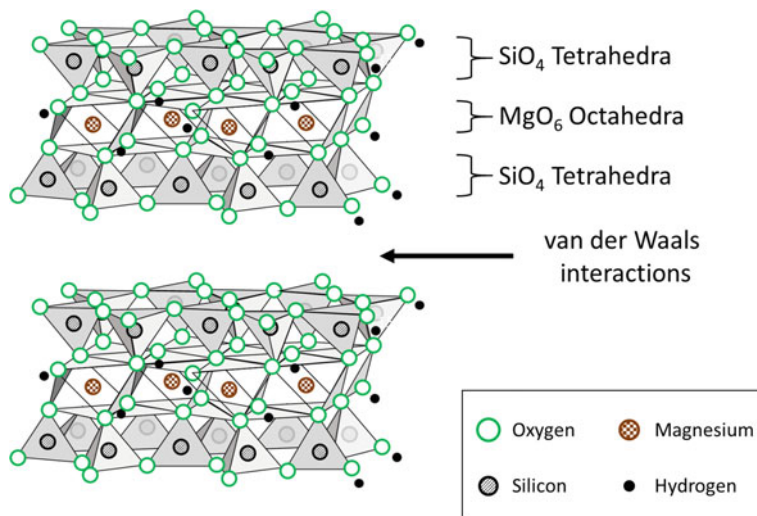


Fig. 9.8 Atomic structure of talc. Adapted from [25]

are referred to as “TOT” sheets (Tetrahedron–Octahedron–Tetrahedron), based on the arrangement of the layers. Each sheet is electrically neutral and so there are no water of crystallization or ions between them. This results in the sheets being held together by only weak van der Waals interactions. The sheets can slide easily over one another, in a similar way to sheets of graphite, and this makes talc an excellent dry lubricant.

The lamellar atomic structure of talc results in most particles being platelets, although fiber forms are also known [26]. An image of a typical talc particle is shown in Fig. 9.9. Particle sizes range from below 1 micron to 15 microns. The smaller particles are referred to as “microcrystalline” and the larger particles as “macrocrystalline” [2, 27]. The particle aspect ratio is partially dependent on the size of the particle, with macrocrystalline particles generally having aspect ratios as high as 35:1 and microcrystalline particles having aspect ratios below 10:1 [2].

Talc affects paint properties in many of the same ways as other platelet extenders. Talc particles orient during drying, lessening mud cracking, decreasing film permeability, and increasing adhesion. It also has a strong effect on paint rheology, increasing viscosity during storage and shear thinning during application. The amount of talc used in paints is commonly below 20%, being limited by its effect of increasing viscosity.

Talc is hydrophobic, which differentiates it from most extender minerals. This hydrophobicity imparts water repellency to paint films. This, in turn, enhances the benefit it brings to anti-corrosion paints. Small-sized talc materials have relatively high oil absorption demand values, which decreases paint CPVC and enhances opacity through dry hide. Despite being hydrophobic, talc is not difficult to disperse if the appropriate wetting agents and dispersants are used.

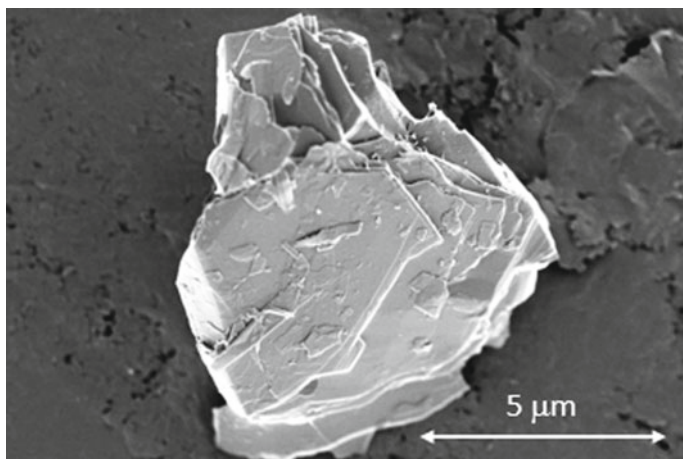


Fig. 9.9 Electron micrograph of a talc particle showing its platelet structure (courtesy of E. Najafi and H. Huezo, Chemours)

In polypropylene and other thermoset plastics, talc shows a good balance between strength and stiffness. It also provides good gas barrier properties and increases heat distortion temperatures [27]. Due to its lubricating nature, it can require extensive melt processing to assure good wet-in and dispersion. Particles with a diameter of less than 5 microns are preferred, although particles with diameter as high as 12 microns can be used. Talc is also valued as a good nucleating agent in polypropylene and nylon, which results in decreased processing times and higher plant throughput.

Mica

The term “mica” refers to a group of 37 similar minerals of which only two, muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$) and phlogopite ($\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$), are of commercial importance. However, only the muscovite form is used by the paints and plastics industries, due to its lower degree of discoloration [28]. It is well known for its sheet-like structure and is typically found as flaky sheets, or books, that can have widths of one meter or more. Raw mica is typically processed by subjecting the mined particles to air jets. This both delaminates (exfoliates) the particles and decreases their median size. For extender applications, these flakes are then wet or dry ground into particles with diameters of 5 microns or greater, making mica one of the coarser extenders [26]. The aspect ratios of particles typically used in paints and plastics are similar to those of talc, although, for some materials, these values are very high (150:1). Mica has a relatively low hardness (2.5 on the Mohs scale—although this can be higher when silica impurities are present) and is basic in water slurries [2].

The atomic structure of mica is based on sheets of tetrahedrally coordinated silicon atoms with intervening octahedral layers of other atoms, similar to talc. Muscovite

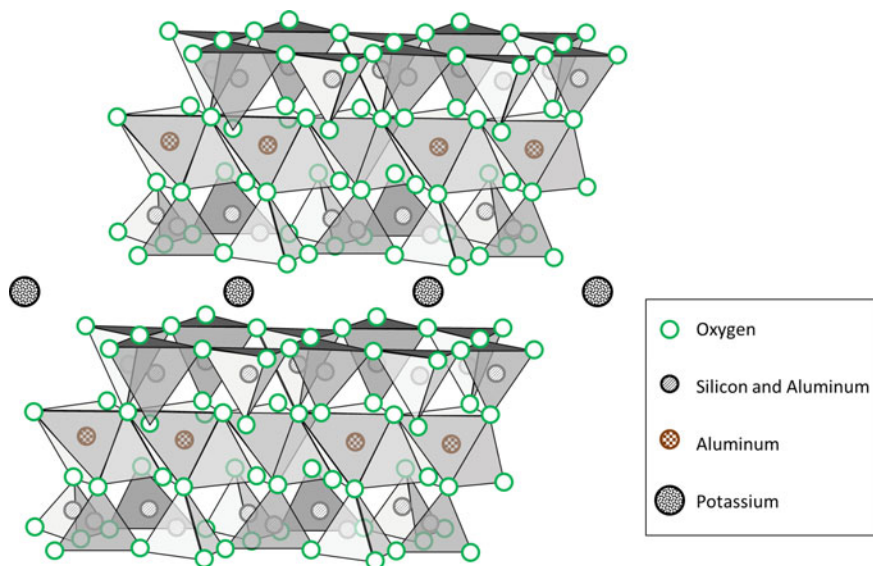


Fig. 9.10 Atomic structure of muscovite mica. Note periodic absences of aluminum atoms in the octahedral mid-layer of each sheet. Adapted from [28]

and phlogopite have different atomic arrangements in the octahedral sheet, due to the different number of cations. In addition, in some forms of mica (including muscovite), some of the central atoms in the oxygen octahedra can be absent. Finally, varying amounts of silicon atoms in the tetrahedral layer can be replaced by aluminum atoms. In all cases, the sheets have a TOT-c structure, where “c” indicates the presence of a counterion between the TOT (Tetrahedron–Octahedron–Tetrahedron) sheets. The structure of muscovite is shown in Fig. 9.10.

The physical differences between mica and talc can be attributed to the presence of counterions in mica. These are required because the sheets in mica are electrically charged, while those in talc are not. Although the counterions in mica increase the bonding strength between the sheets (electrostatic forces are stronger than van der Waals forces), the bond strengths between the sheets are weaker than those within the sheets. This allows the sheets to be easily delaminated, although not to the same extent as those in talc.

The properties that mica confer to paints are similar to those of other platelet particles. Mica modifies rheology, minimizes settling, reinforces both the drying paint and the dry paint film, promotes corrosion resistance by the paint, improves film strength (for example, scrub and abrasion resistance), enhances film durability, and improves film adhesion. Mica has a distinctive sparkle appearance. Although this property is used advantageously to create special effect pigments (see Chap. 8), it is not always welcomed in paints. Overall, mica tends to be used only at relatively low concentrations in paints (5% or less of the total extender quantity).

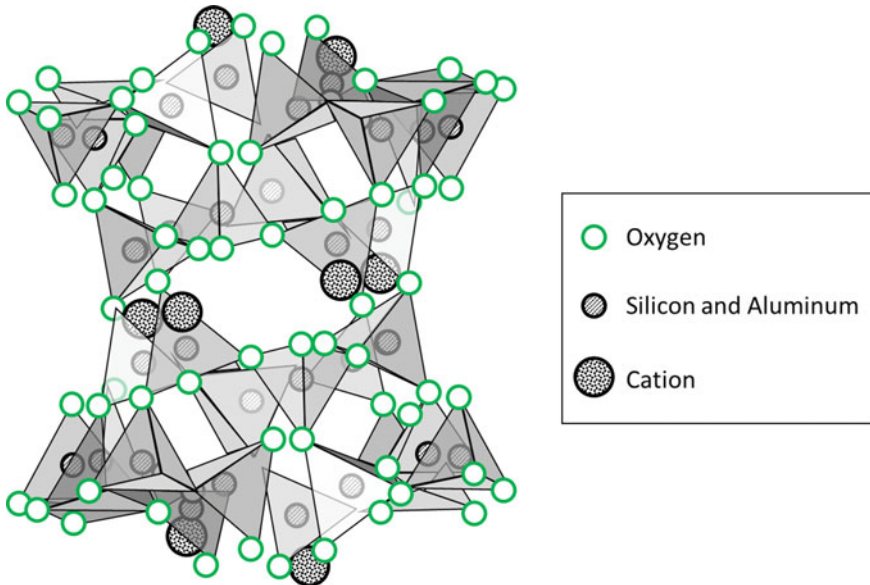


Fig. 9.11 Atomic structure of feldspar. Tetrahedra are centered around either silicon or aluminum atoms. In anorthite, half of these are aluminum atoms, while in albite and microcline, a quarter are aluminum atoms. Adapted from [31]

Mica is valued in the plastic industry for its reinforcing properties [29], as well as its ability to increase the heat deflection temperature, decrease warpage, and reduce shrinking [30]. It also attenuates sound, which is desirable in automotive applications. The most common plastic application of mica is in polypropylene, where it is valued for its strong reinforcement and high dimensional stability. Mica has a high surface polarity, which decreases its compatibility with many polymers. This can cause poor adhesion between the polymer and particle, resulting in void formation at these interfaces, accompanied by a reduction in film strength. This incompatibility also affects the dispersibility of the particles. Surface treatments with silanes can minimize these deleterious effects [30].

Feldspar

Feldspars are the most abundant family of minerals, accounting for more than half of the earth's crust. There are over 25 feldspar mineral types, but only three are used as fillers—orthoclase (KAlSi_3O_8), albite ($\text{NaAlSi}_3\text{O}_8$), and anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$). Nepheline syenite is a related, but less pure, feldspar-like material that is often classified with the feldspars. Deposits of nepheline syenite are much less common than feldspar. Feldspars are generally known for their blocky structure and high hardness (6.0 on the Mohs scale). This level of hardness limits the degree to which these

particles can be ground and can cause excessive equipment wear, both when it is processed and when it is used. However, this hardness translates to better strength in plastics and provides surface toughness to paints. Feldspars generally have adequate brightness for most paint and plastics applications. Due to their blocky structure, feldspars have lower surface areas, oil absorption values, and binder demands than non-blocky extenders with the same particle size.

The blocky nature of feldspar is a consequence of its three-dimensional, space-filling structure. This can be contrasted to the platelet shape of kaolin, talc, and mica, and is similar to calcium carbonate and silica. The atomic structure of feldspars consists of silicon and aluminum oxide tetrahedra joined together, through bridging oxygen atoms, into four-membered rings (Fig. 9.11). These rings are arranged in chains that join other chains that are oriented in different directions. This structure is similar to that of quartz (discussed below).

The oxide network in feldspar is negatively charged. This is due to the difference in electrical charge between the silicon (+4) and aluminum (+3) atoms—each aluminum atom in feldspar must have an associated counterion. The excess negative charges are balanced by different cations in the different feldspar minerals. In many cases, these cations are present as a mix, creating solid solutions. The counterions are located in cavities between the intersecting chains. The presence of counterions produces cleavage planes in feldspar.

Feldspar offers many benefits to paints. Its blocky shape allows it to be used at high concentrations, and its hardness confers good scratch and abrasion resistance to the paint film. Because feldspar is transparent in the ultraviolet, it can be used in radiatively cured paints. In addition, it generally improves paint brightness and durability. Balanced against these advantages are the limited degree to which these particles can be ground—typically the finest particles are 2 to 3 microns [2]—and their hardness, which is undesirable in many paint applications.

The hardness of feldspar also restricts its use in plastic applications. Its refractive index (between 1.50 and 1.55) gives it greater transparency in most polymers than any other filler at an equal concentration [32]. It can be used in films at low levels (0.1 to 1% by weight) as an anti-blocking agent [33]. It also has been used for greenhouse glass as it readily passes visible and ultraviolet light but reflects infrared light. This prevents greenhouses from overheating during the day and overcooling at night [34].

Wollastonite

Wollastonite is a calcium silicate with the chemical formula CaSiO_3 [35]. Deposits are not as widespread as those of the other extenders considered here—for example, there are only two mines in the United States, and they are located only a few hundred kilometers from one another [36]. Unlike the other silicates discussed so far, though, wollastonite particles are acicular. Their aspect ratios fall into two groups. The “powder” grades have aspect ratios between 3:1 and 5:1 while the “HAR” (High Aspect Ratio) grades have ratios that vary between 12:1 and 20:1. Grades used as paint or plastic extenders can be up to ten microns in their long direction.

Wollastonite is a relatively new mineral extender, having first been commercialized in the mid-twentieth century [37]. Its importance rose in the 1970s and 1980s when the negative health effects of asbestos became fully understood. Due to its acicular shape, wollastonite became a substitute for short fiber asbestos during that time [36]. Wollastonite is available in relatively pure form (97 to 99%), giving it good brightness and low discoloration. Wollastonite is the only white acicular extender currently available in industrial quantities.

The pH values of wollastonite slurries can be as high as 11, which is quite unusual for an extender. This is because in water a coating of highly caustic calcium hydroxide forms on the particle surface [36]. Wollastonite is moderately hard, with a Mohs value ranging from 4.5 to 5.5. Since it is anhydrous, it evolves little water when heated (weight loss at 1,000 °C is between 0.5 and 2.0%). Although it is anhydrous, overgrinding this material causes it to partially hydrate due to water absorption onto the freshly reated surfaces. In addition, overgrinding reduces the needles to nodular particles, resulting in a loss of many of the desirable properties that are due to its acicular shape.

Wollastonite's acicular particle shape is a consequence of its atomic structure. Wollastonite is composed of oriented one-dimensional, corner-sharing SiO_4 tetrahedra (Fig. 9.12). Calcium counterions reside in cavities between these chains. An electron micrograph of a wollastonite extender particle is shown in Fig. 9.13.

Wollastonite is used as a flattening agent and suspension aid in paints. In comparison to other silicates, it has a low binder demand and minimal effect on paint viscosity. These properties allow it to replace greater amounts of paint resin than is possible with the other silicates. Wollastonite is used to impart roughness, scrub and scratch resistance, hardness, adhesion, and durability to paints. Its high alkalinity gives it good corrosion protection properties, and it can synergistically enhance the anti-corrosion performance of other inhibitor pigments [38, 39]. Corrosion resistance is perhaps its most important property for the paint industry.

The largest industrial use of wollastonite is as an extender in plastics [36]. Due to its acicular shape, it can replace glass fibers in some fiberglass applications. Here it is valued for its lower hardness and abrasivity than glass, which has a Mohs hardness of 7. Fine particle size grades can be used for imparting scratch resistance. Wollastonite is valued in automotive plastics applications for giving strength, impact resistance, and dimensional stability. Wollastonite grades used in plastics, and in some paint applications, are often surface treated with bifunctional silanes. This imparts excellent plastic reinforcing performance, since it strengthens the interactions between the particles and the surrounding matrix.

Precipitated Aluminum Silicate

As nature shows, there are a very large number of ways that aluminum and silicon can combine to form stable oxide structures. The energetic favorability of solid aluminum silicates is so great that mixing solutions of sodium aluminate and sodium silicate results in a violent release of heat and the near-instantaneous formation of a

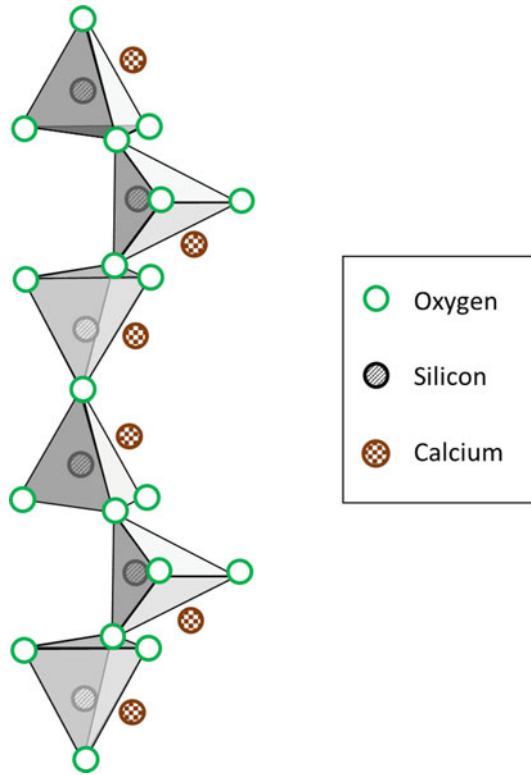


Fig. 9.12 Atomic structure of wollastonite. Adapted from [37]

voluminous, bright white solid mass. Many forms of precipitated aluminum silicates are useful as extenders. We will not review the entire gamut of them here, but will mention some commonalities that they have.

Like all synthetic extenders, the precipitated aluminum silicates are characterized by their high purity and the resulting high brightness and low yellowness. The mean particle size varies from type to type, but is generally low, with some materials being less than 0.10 microns in diameter. Size is often difficult to measure because these materials tend to be at the lower limit of many types of size measuring technologies (see Chap. 2). Most precipitated aluminum silicates are nodular because their chemical bonds extend in three dimensions, similar to feldspar and silica.

Like other small particles, these materials have high surface areas, high oil absorption values, and high binder demands, and so they strongly influence paint and polymer melt viscosity. This limits their use to 5% or less in paints. Due to their small size, precipitated aluminum silicates allow for more optimal spacing of TiO_2 pigment particles than most extender particles (see Chap. 16). This increases opacity

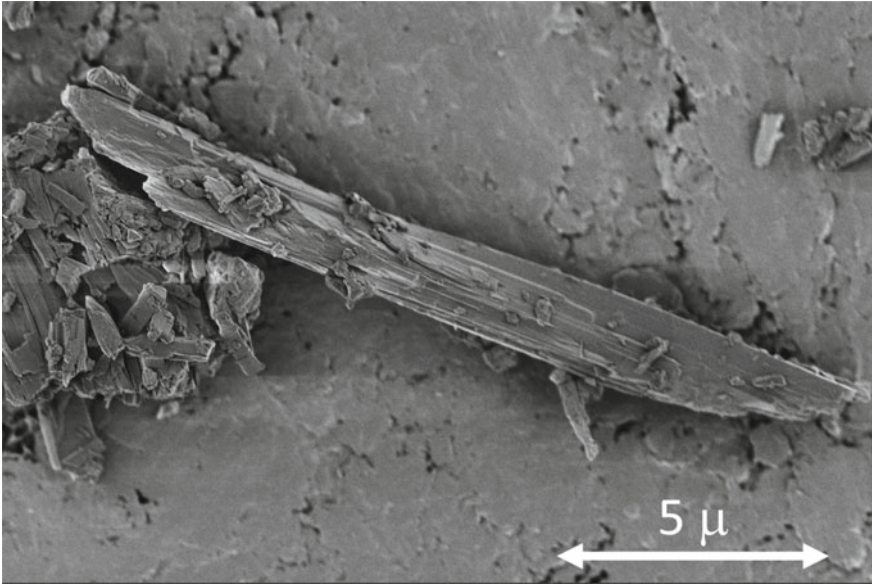
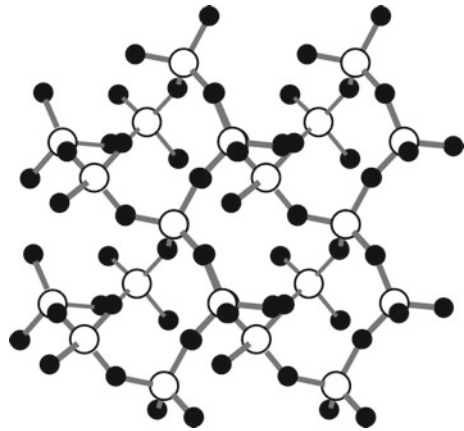


Fig. 9.13 Micrograph of wollastonite showing its acicular structure (courtesy of E. Najafi and H. Huezo, Chemours)

Fig. 9.14 Ball and stick schematic representation of the three-dimensional network of SiO_2 tetrahedrons found in quartz. The white balls are silica; the black balls are oxygen



both below and, especially, above the CPVC of a paint, which contributes significantly to dry hide.

Silicas

Pure silica has the chemical formula SiO_2 . It is most commonly found in nature as the mineral quartz and, less commonly, the mineral cristobalite. It is also found in a variety of amorphous forms. Impurities in amorphous silica can impact its color and structure, such as seen in opals and obsidian. The different forms of silica are often found as sands, and together they comprise roughly 10% of the earth's crust. The distinguishing characteristics of silica are its high resistance to heat and chemicals, and its extreme hardness (7 on the Mohs scale).

A wide variety of silica extenders are available to the paint and plastics industries. These differ in particle shape, particle size, agglomerate structure, purity, and means of manufacture (natural, precipitated or fumed). The major types of silica extenders are quartz and diatomaceous earth, both of which are natural, and fumed and precipitated silicas, both of which are manufactured.

The atomic structure of silica is quite simple, consisting of a three-dimensional array of silicon atoms that are tetrahedrally bound to four oxygen atoms. Each oxygen atom is bound to two silicon atoms, resulting in bridges between the silica-centered tetrahedra (Fig. 9.14). In amorphous silica, the local tetrahedral structure surrounding the silica atoms is unchanged, but the tetrahedra are not aligned in the regular arrangement as they are in quartz and cristobalite. In all forms, the surface terminates with a mixture of Si–O–Si bridges and Si–OH hydroxyl groups. The surface hydroxide groups bond strongly to silanol- or siloxide-based organic surface treating agents.

Quartz

Quartz is the main component of many sands and as a result is a very abundant mineral. It is typically found as particles that are too large for extender use, although some deposits of microcrystalline silica are known. Quartz can be comminuted to extender sizes using typical grinding processes, but due to its hardness, it is not ground to sizes below 2 microns [2]. Care must be taken, both in manufacture and use, to avoid discoloration (graying) due to the wear of metal equipment.

Quartz particles are typically blocky or nodular, as expected based on their three-dimensional atomic structure (Fig. 9.14). The nodular shape and relatively large particle size give quartz low surface areas and low oil absorption values. This allows for high loadings in paints without significantly altering viscosity. Quartz is often found in water-borne paints that use silicate binders in place of organic resin. Here, the dissolved silicate bonds strongly with the quartz surface as the paint dries. Quartz is also used in thick coatings to give high wear resistance [2], and in anti-corrosive paints to enhance substrate protection. The noticeable yellow cast of natural quartz often prevents its use in bright or white coatings.

Quartz is not typically used in plastic applications.

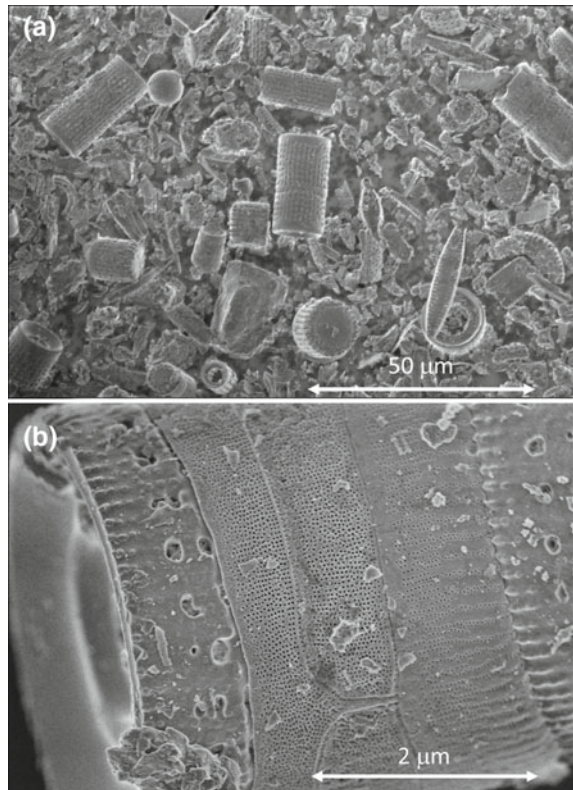
Diatomaceous Earth (Kieselguhr)

Diatomaceous earth, also known as kieselguhr or diatomite, is a unique material. While its composition is amorphous silica, which is not unusual, its shape is not like any other mineral (Fig. 9.15). Diatomaceous earth is formed by the fossilization of the skeletons, or shells, of single-celled phytoplankton called diatoms. The structure of the original shell is preserved in the fossilization process. These structures are defined not only by their extraordinary shapes, but also by their extreme porosity (note the different pore structures and sizes in the different particles shown in Fig. 9.15).

Over 12,000 thousand species of diatoms are known, leading to an enormous array of shapes and sizes. The particle size is unique in the sense that it is determined biogenically, rather than through geological processes or comminution during processing. Grinding to smaller particles, in fact, leads to a loss in many of the unique properties for which diatomaceous earth is used.

Each deposit of diatomaceous earth is unique, both in the mixture of diatom structures and the nature of any impurities. The shape of a diatom is determined by its species, which, in turn, is dependent on the geographical conditions when the diatom was living and the age of the deposit. Different deposits can vary in brightness

Fig. 9.15 Electron micrograph of diatomaceous earth. **a** Assortment of shapes. **b** Assortment of pores (courtesy of E. Najafi and H. Huezio, Chemours)



as well as age, and darker materials are often calcined to improve brightness. This also reduces the surface area and converts the initially amorphous silica into crystalline silica (quartz).

Regardless of their shape and composition, diatomaceous earth particles always have a characterized by its very low density, which is attributable to their very high porosity. In addition, being composed of silica, it is very abrasive, with a Mohs hardness value of 6 (somewhat less than quartz). This unique blend of properties allows diatomaceous earth to be used in a wide range of applications, including toothpaste, catalyst supports, and liquid absorbent in addition to its broad use as an extender in paints and, to a lesser extent, plastics.

The combination of large particle size (2 to 20 microns) and high oil absorption (100 to 150 g oil per 100 g particles) make diatomaceous earth a useful flattening agent in paints. It is typically used for this purpose at levels of only a few weight percent [26]. Higher levels do not further decrease paint gloss but instead result in a large increase in paint viscosity, as a result of the high oil absorption of the material. Its high oil absorption also results in a strong reduction of the CPVC of a paint, which is advantageous in paints formulated above the CPVC for dry hide (Chap. 4).

Diatomaceous earth also helps maintain other particles in suspension and gives good brushability to the liquid paint. Its porosity allows paints to dry quickly and uniformly. It enhances the adhesion of paints to the substrate as well as improves tooth in undercoats (i.e., the interlayer adhesion). However, unlike many extenders, diatomaceous earth generally weakens the paint film. In addition, it is generally too yellow to be used in bright or white coatings.

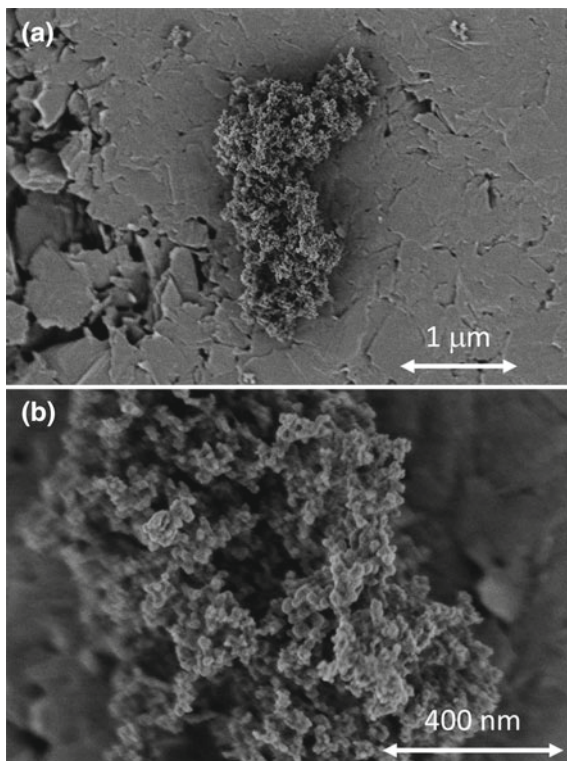
In plastic film applications, diatomaceous earth is used at low levels as an anti-blocking agent.

Fumed Silica

Fumed or pyrogenic silica, as the name suggests, is produced by a flame process in which an aerosol of silicon tetrachloride is hydrolyzed with water. This process is similar in some ways to the chloride process for titanium dioxide, where titanium tetrachloride is reacted in a flame to produce the oxide (see Chap. 7). However, for fumed silica, the oxygenation species is water, resulting in hydrochloric acid as a by-product, whereas in titanium dioxide, the oxygenation species is oxygen, resulting in chlorine gas as a by-product. This gas is returned to the earlier stages in the titanium dioxide process.

The primary particle size of fumed silica ranges from 7 to 40 nm. However, individual primary particles do not survive the flame process and are instead joined into various structures. These structures consist of aggregates, with sizes of around 120 nm, which, in turn, join together into looser agglomerates, which are typically greater than 1 micron [40]. The primary particles and agglomerate structure of fumed silica are shown in Fig. 9.16. In many ways, the structure found in fumed silica is similar to that of carbon black, which is also made by a flame process (see Chap. 8).

Fig. 9.16 Electron micrograph of fumed silica under **a** magnification of $25,000\times$ and **b** magnification of $100,000\times$ (courtesy of E. Najafi and H. Huezio, Chemours)



Fumed silica has an extremely high surface area (between 50 and $400\text{ m}^2/\text{g}$) and an extremely low bulk density (0.03 g/ml). This density is so low that fumed silica must be compressed or granulated for handling purposes. This can be a challenge since over-compression can result in difficulties in dispersing the particles into a liquid paint or plastic melt. The surface silanol groups give fumed silica a hydrophilic character, although various organic post-treatments can make the particles hydrophobic.

In coatings, the very high surface area and the propensity to form large, three-dimensional networks via weak hydrogen bond linkages make fumed silica an effective rheological control agent at levels between 0.4 and 2.0 percent. Its high hardness improves the scratch and abrasion resistance of dry paint films, and its chemical inertness is an advantage in anti-corrosion paints.

Fumed silica also finds use in paints as an effective flattening agent [41]. Due to its small size, fumed silica particles readily migrate to the paint film surface during drying. There the particles reduced surface smoothness. Fumed silica also enhances dirt pick-up resistance due to its location on the film surface.[40] It is also used at levels below 1% as a flow aid in powder coatings. In this capacity, it shortens dispersion and melt times.

Fumed silica is used in plastics to adjust rheology and to provide anti-blocking for plastic films. It is also used in some niche plastics applications [42]. It is not used in plastics as much as precipitated silica is (discussed next), due to its higher cost.

Precipitated Silica

Precipitated silica is produced by the neutralization of a silicate salt solution. The resulting particles are in many ways similar to fumed silica particles, having high surface areas, high oil absorption values, high binder demands, and low bulk densities. An important difference between these forms of silica is the higher amounts of water in the precipitated material—up to 7%, with as much as half of that being surface hydroxyl groups [42].

Precipitated silica is formed as round or blocky particles with a median particle diameter between 5 and 100 nm. However, agglomerates as large as 100 microns can form when the particles are dried. These large particles can be ground to diameters between 1 and 40 microns. Like fumed silica, precipitated silica has a very low bulk density and must be compressed or granulated for handling purposes.

The high levels of surface hydroxyl groups make these particles quite amenable to silane surface treatments. These alter the hydrophobic/hydrophilic balance of the particles, allowing them to be optimized for specific organic matrices. They are also sometimes treated with waxes for the same reason. Surface treatments are typically done at levels between 5 and 15% [43].

Precipitated silica is employed in paints for many of the same reasons as fumed silica. It is, however, more likely to be used as a flattening agent, and less likely to be used as a rheology modifier, as fumed silica is. In plastics, it is used to enhance strength (its largest single use is to enhance the strength of rubber tires). It is also used to modify the rheologic properties of polymer melts. Recent advances in surface treatment have significantly improved the dispersibility of precipitated silica in plastics [42].

Barium Sulfate

Barium sulfate can be used as an extender in both its natural form (barite) and in synthetic form (blanc fixe). It is a salt with a structure consisting of discrete ions extending into three dimensions. This results in a nodular or blocky particle. Barium sulfate is relatively soft, with a Mohs hardness of 3.

Barium sulfate has two features that distinguish it from other extenders. First, it has a significantly higher density (4.4 g/ml) than all other common extenders (these vary from roughly 2.5 to 3.0 g/ml—refer to Table 9.2). Second, it has a refractive index of 1.64, which is higher than other extenders and of resins or polymers. While this is not high enough for barium sulfate to be classified as an opacifying agent, it does offer a limited degree of light scattering.

Natural barium sulfate extenders are typically comminuted to sizes between 1 and 15 microns through either wet or dry grinding processes [26]. The particles are nodular, as mentioned above, and the combination of relatively large size and high density gives barium sulfate extenders lower surface areas (1 to 4 m²/g) than most other extenders. This also gives barite a low oil absorption value (roughly 15). Synthetic barium sulfate, known as blanc fixe, has a medium particle size ranging from 0.7 to 4 microns, depending on the synthesis conditions. The process for making blanc fixe is discussed in the section on synthetic extenders below.

Barium sulfate is used in coatings for similar reasons as other nodular particles. Although the high density of barium sulfate is an advantage in some ways, it is a disadvantage in others. It settles easily, and it significantly increases the density of paint. This is economically unfavorable in most paint markets, since paint ingredients are purchased on a weight basis and typically sold on a volume basis. Unlike many extenders, blanc fixe can be used in gloss paints as it does not roughen the film surface. It improves the toughness of a paint film, and its chemical resistance is valued in anti-corrosion paints.

Barium sulfate is used in the plastics industry, where its density confers good vibrational mass dampening. Its high density also suggests solidity and good quality to plastic consumers. Blanc fixe is also used in high concentrations in polypropylene or polystyrene for X-ray shielding applications.

Calcium Sulfate

Calcium sulfate was at one time used extensively in the coatings industry. A blend of calcium sulfate and titanium dioxide was also popular, both to the TiO₂ manufacturer (as a way of disposing of sulfate by-product from the sulfate manufacturing process [44]) and to the paint manufacturer (as a way of decreasing the cost of opacity). However, this was at a time when paints were predominately solventborne. Calcium sulfate is soluble enough in water to create problems in water-borne paints [43], and the production of these calcium titanate pigments, as they were known, was discontinued in the early 1970s [45].

Calcium sulfate is used as an extender in plastics, where its main value is as a simple economic substitute for polymer.

Production of Mineral Extenders

Extenders originate from natural minerals and rocks that can be mined either in the open air or underground. Once the materials of interest are removed from the earth, they are broken apart into ever-finer particles, initially by mechanical crushers, and then through wet or dry grinding. In some cases, the material is separated on a size basis during or after this process. A small fraction of extenders (the synthetic

extenders) undergoes additional processing. This typically involves, in this order, the reaction of the raw material to a new material, purification (in some cases), then reaction to the desired material. These reactions are run under very tightly controlled conditions, resulting in particles with high purity, controlled size, and enhanced functionality. In general, the smaller size extenders, such as precipitated calcium carbonate, barium sulfate, and silica, are made synthetically, while larger size extenders are manufactured directly from the mined minerals [3].

Natural Extenders

Mining is an essential aspect of extender production. The first step in the mining process is prospecting. During this phase, a number of aspects of the potential mine site are evaluated, including the extent and quality of the deposit, the thickness and composition of any overburden that must be removed, and the probable equipment needs and process steps to extract and purify the desired material. In addition to these technical and economical evaluations, consideration must be given to local, regional, and national government regulations, as well as existing regional infrastructure.

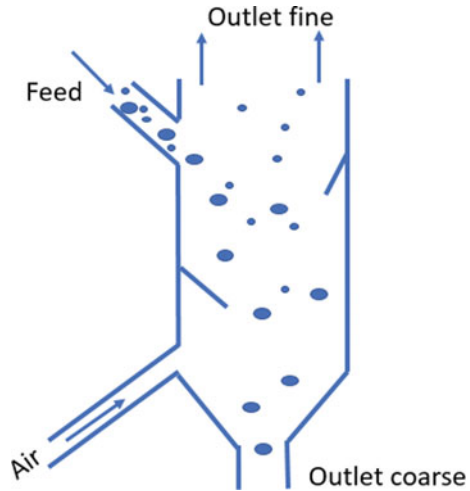
The installation of the mine begins once the prospecting phase has been successfully completed. The most appropriate mining techniques are evaluated and selected to match the specific site details. Typical equipment includes bucket-wheel and shovel excavators, conveyor belts, heavy-duty trucks, etc. The mining of highly compacted materials may require the use of explosives. All in all, several years can typically elapse between initially identifying a potential mine site and finally extracting the first shovelful of mineral from the ground.

Once mining commences, the material is removed and mechanically crushed to particles with diameters from 100 to 300 mm. After the physical removal of loose soil, detritus, and substandard material, the remaining material may be washed, ground, filtered, wet or dry milled, and classified, resulting in the final extender product. During the purification process, ferrous impurities, which often discolor the final product, may be removed via a magnetic separator.

Both dry and wet grinding can be used to reduce particle size. Dry grinding, which is typically done in ball mills, can cost-effectively reduce particles to a median diameter as low as 1.5 microns, depending on the material. For smaller particles, wet grinding becomes more economical despite the extra energy required to separate water from the material and then dry it. In the wet grinding process, an aqueous slurry with a high solid content is fed into ball mills that are designed to work with slurry materials. These mills can grind the particles to sizes below one micron. When the particles have the desired diameter, the material is dewatered, dried, and packaged. Alternatively, it can be delivered as a slurry, which avoids the water separation and drying steps.

Air classification is an essential aspect of the dry grinding process in many extender mining operations. There are several variants of air classifiers, but they are all based on the premise that small particles, having a large surface area on a

Fig. 9.17 Schematic representation of an air classifier



weight basis, have greater air drag than large particles. The mix of ground particles is gravity fed through the side a chamber with a current of air blowing upwards. The smaller particles are entrained in the rising air stream and exit through the top of the chamber, while the larger particles fall to the base of the chamber and are returned to the mill (Fig. 9.17). The entrained particles are collected vertically from the air stream that exits through the top of the chamber. These particles can be classified by size according to the height they reach in the exiting air stream.

Some extenders undergo thermal processing, which can significantly improve many properties. This can be illustrated with the heat treatment of kaolin. Calcined, or anhydrous kaolin is produced by heating wet-ground kaolin to high temperatures. The dehydration process occurs in stages [46]. Between 450 and 650 °C, approximately 90% of the waters of crystallization are removed, converting the kaolin into an amorphous material called metakaolin. Metakaolin is used extensively in the cement industry, but not as an extender for paints or plastics. Further heating to between 900 and 955 °C removes the remaining water and converts the material to a spinel phase that can be used as an extender in paints and plastics. The hot material is cooled, then ground to undo the agglomeration that occurs during the calcination process. The calcination process increases purity, decreases discoloration, and alters the particle size and shape.

Flash calcination is a special variant of the calcination process that is unique to kaolin clay. In this process, ground kaolin is heated at rates between 10^3 and 10^5 degrees per second over a very short time (typically a few tenths of a second), then quenched at similar rates of cooling [47]. Under these conditions, dehydration is not complete, but the material is in a different form than when it is incompletely dehydrated through conventional calcination. Instead of creating metakaolin, the flash calcination process expands the platy structure of the kaolin particles and, at the same time, anneals the surfaces of the particles, which are heated the most, into a

glassy structure. This seals the voids that are formed by the exiting water vapor and result in an amorphous particle that contains very small internal air cavities. These air cavities scatter light in end-use applications, improving opacity and allowing for a decrease in TiO_2 content. They also contribute to the wet hide of paint.

Synthetic Extenders

Many minerals that are formed naturally can also be synthesized artificially. The starting material for this process is often the same mineral that is being synthesized. For example, mined calcium carbonate is used as the starting material for synthetic calcium carbonate. The reason for doing this process is that the synthetic mineral can have higher purity (and less discoloration), a lower average particle size (and tighter size distribution), or both.

Although the synthetic details differ from one extender to another, nearly all follow the same strategy. The raw mineral is first reacted chemically to form a new species that contains the element of interest. This new species is, optionally, purified, and then is reacted a second time to return it to its original composition. This conversion process is well controlled in order to form the proper crystalline phase, the desired median particle size, and the optimal particle size distribution. This is similar in concept to the manufacture of pigmentary titanium dioxide (Chap. 7), where the titanium content of the ore is transformed into titanyl sulfate or titanium tetrachloride, purified, and then reacted to form pigmentary TiO_2 particles.

Precipitated Calcium Carbonate

Precipitated calcium carbonate (PCC) is typically made by a three-step process. During the first step, CaCO_3 (limestone) of high purity is heated above $900\text{ }^\circ\text{C}$, where it decomposes into calcium oxide (lime) and CO_2 . The carbon dioxide is collected to be used in the final step of the process, while the lime is immersed in water as the second process step. This produces a calcium hydroxide (slaked lime) suspension. In the third step, the CO_2 that was formed in the first step is added to this suspension, resulting in the deposition of the precipitated calcium carbonate particles. By adjusting reaction variables such as pressure, temperature, time, and the presence of chemical additives, the particle shape and size distribution can be controlled. Grinding or separation via classification may be necessary to produce the final extender material.

Precipitated Barium Sulfate

Blanc fixe, or synthetic barium sulfate, is produced in a two-step process from the mineral barite (BaSO_4). First, barite is reacted with coke (carbon) at high temperatures, producing barium sulfide (BaS) and carbon monoxide. The barium sulfide is purified, dissolved in water, and reacted with a sulfate source such as sulfuric acid.⁴ Barium sulfate is completely insoluble in water⁵ and precipitates as a fine white powder.

Physical properties such as median particle size, particle size distribution, and shape are controllable using production process parameters such as concentration, temperature, agitation, pH, and aging time. Once the desired precipitate is formed, it is purified by filtration and washing, often multiple times. In the last step of production, the material is dried and ground to break up the agglomerates that form during drying. Blanc fixe particles are controlled in the range of 0.7 to 4 microns, making them smaller, and their particle size narrower, than the original barite particles [1]. They are also significantly brighter than their natural counterparts, allowing them to be used in bright paints.⁶

Surface Treatment of Extenders

The surfaces of most natural extenders are hydrophilic, allowing for easy dispersion in water-borne paints. However, a hydrophobic surface can be advantageous in plastics and in some paint applications. In plastics, a hydrophobic surface would be more compatible with the polymer matrix, similar to the principle that “like dissolves like”. In the same way, a hydrophobic particle would be more compatible in a non-polar paint system. In addition, a hydrophobic particle can make the paint film more water-resistant. The use of hydrophobic particles is significantly more common in plastics applications than paint applications.

For these reasons, extenders are often treated with an organic, hydrophobic agent as a final stage in their production. These agents modify both the particle–particle and particle–matrix interactions. While the particle–matrix interactions are usually the more important, the change in particle–particle interactions affects the bulk flow and bulk density of the extender, as well as its dustiness.

The modifiers used for plastics applications can be classified into two groups—coupling surface modifiers and non-coupling surface modifiers [48]. This distinction

⁴ Lithopone is a related white pigment that was used extensively before pigmentary TiO_2 was developed commercially. It is made by combining a barium sulfide solution with a zinc sulfate solution. Barium sulfate and zinc sulfide simultaneously precipitate from this mixture.

⁵ The insolubility of barium sulfate can be demonstrated by its use as an X-ray contrast agent. Although soluble barium is quite toxic, barium sulfate can be safely ingested or otherwise entered into the body with no ill effects.

⁶ The low hardness of barium sulfate also contributes to paint and plastics brightness because these soft particles do not abrade production equipment, which would discolor the paint or plastic.

is made according to the type of modifier/polymer interaction. Non-coupling modifiers are too short to enter into the polymer phase and so affect only the wettability and dispersibility of the particles. The effect of wetting has been the subject of debate [6, 48], but it appears to be negative—the surface modifier decreases the surface energy of the extender particles [49], while wetting is greatest on high energy surfaces [50]. The non-coupling modifiers include fatty acids such as stearic acid and its derivatives, and also some silanes with short alkane chains. Most of the surface-treated extenders that are used in the paint industry are coated with fatty acids.

Coupling modifiers, on the other hand, partially enter into the plastic matrix. An interphase region is believed to exist within the polymer that is near the particle surface. This region is especially important for the incorporation of particles with high surface energy (e.g., non-surface treated particles) into the polymer melt [6]. This region has properties that differ from the bulk polymer, and it is believed that coupling modifiers on the particle surfaces can diffuse into this region, strengthening the interaction between the particle and resin. The thickness of this region varies with the identity of the particle and the polymer, and is believed to range from one nanometer to over one micron.

Coupling modifiers are very similar in concept to the dispersant molecules used to stabilize particles in liquid paints (Chap. 11). They consist of two parts—a head and a tail [48]. The function of the modifier head is to bond to the surface of the particle. There are two types of heads—reactive and non-reactive. The reactive heads chemically bond to the particle surface, while the non-reactive heads do not. Reactive heads are often composed of silanols or alkoxy silanes, which can react with a surface hydroxide, releasing a water molecule. Carboxylic acid groups can also be used for this function. The tails are typically long alkyl chains, sometimes with reactive moieties that can form chemical bonds with the polymer.

Summary

Extenders exist in a wide range of chemical compositions, shapes, particle sizes and size distributions, and physical and chemical properties. This results in an equally wide range of interactions with and uses in paints and plastics, going beyond the traditional role of extenders as particles that simply fill a paint or plastic, lowering its cost. The functionalities that these particles can bring to paint or plastic include enhancing processability, altering the rheology of liquid paints and molten polymer, preventing sedimentation of paints, improving various strength attributes (crack resistance, scratch resistance, tensile strength, stiffness, etc.), increasing weatherability, improving corrosion resistance, and enhancing certain optical properties (particularly dry hide and gloss in paints).

Extenders can be conveniently categorized according to their mineral composition. The major categories of extenders are the carbonates (which are the most commonly used extenders in paints and plastics), the silicates, the silicas, and finally insoluble salts. The particle shape is a function of the atomic arrangement within the

crystal lattice. Particles with bonding interactions extending in all three dimensions are nodular or blocky. Those for which strong bonding interactions extend only in two directions, with weak hydrogen or van der Waals bonding in the third direction, are platy or lamellar, while those for which strong bonding interactions occur through one-dimensional chains are needle-like or acicular.

The origins of all mineral extenders are geological deposits. Extenders are extracted from the ground, then physically separated from other materials, such as loose soil or other detritus. Most extenders undergo grinding and size classification. Impure extenders can be processed by reactions that convert them to an alternate chemical, then back reaction to the original mineral. This allows for additional purification and for control of median particle size, particle size distribution, and, in some cases, particle shape. While this additional processing comes at a cost, in some applications, this cost is more than offset by the improved properties.

Additional details about the utility of extenders in paints and plastics formulations can be found in Chap. 16 (for paints) and Chap. 17 (for plastics).

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