Chapter 7
White Pigments

Contents

Introduction

Chapters in this book discuss entire classes of materials—color pigments (Chap. 8), extenders (Chap. 9), and resin particles (Chap. 10). Yet here we devote nearly an entire chapter to only one material class—titanium dioxide pigments. This seeming imbalance is fully justified by a number of factors. The first is the volume of TiO_2 pigments sold annually. It is estimated that on a weight basis TiO_2 accounts for about two-thirds of all pigments used annually. On a value basis, it accounts for roughly 44% [1].

M. Diebold et al., *Pigments, Extenders, and Particles in Surface Coatings and Plastics*, https://doi.org/10.1007/978-3-030-99083-1_7

In addition, it is used in nearly all opaque paints and plastics (the exception being black), and at levels significantly higher than that of the pigments that provide color. For example, a high-quality light blue paint may contain 300 g of TiO_2 per liter (2.5 pounds per gallon) but only a few grams of blue pigment per liter. This disparity is due to the different ways that these particles interact with light. Light scattering by the TiO_2 is much weaker than light adsorption by color pigment particles, as discussed in Chap. 3.

Finally, unlike extenders and color pigments, for which there are a multitude of choices for any given paint or plastic, there are only two materials that provide whiteness, brightness, and opacity—TiO_2 and air. Other white pigments were used in the past, but today none can compete with TiO_2 in respect to its high scattering strength and non-toxicity.

TiO_2 can be considered a specialty chemical in the sense that it must be customized for each specific end-use application. One size does not fit all, and using the TiO_2 grade in an application for which it was not designed will cause a significant reduction in its opacity performance, as well as likely resulting in the degradation of other end-use properties.

There are two processes for making the TiO_2 particles themselves—the sulfate process and the chloride process. Once made, the particle surfaces are modified to enhance certain attributes of the pigment or the material into which the pigment is incorporated. In this chapter, we discuss these aspects of manufacture as well as the end-use properties that can be controlled by the pigment producer.

Pigment Manufacture

The physical and chemical properties of small particles discussed in Chap. 1 are dictated by the chemical nature, surface properties, and dimensional characteristics of the particles. Properties such as size, shape, and purity of pigmentary TiO_2 are controlled by the production process. There are two different commercial processes for producing pigmentary TiO_2: the sulfate and the chloride processes.

In both cases, the process for its manufacture begins with mining the ore, and upgrading its value by doing physical separations from other minerals that are present with it. These separations are typically made on a size, density, magnetic, or electrostatic basis. In addition, the iron content of the ore, often present as an iron titanate rather than separate iron species, can be reduced by slagging or other chemical means. Together these processes are often referred to as ore beneficiation and can increase concentration of the desired particles from a few percent to upwards of 90%. The benefits of beneficiation of the ore are that it decreases the amount of material that is shipped to the ultimate manufacturing site and the amount of material that must be reacted and disposed of at that site. There is also environmental advantage that the removed impurities are still in their natural state and so can be directly returned to the environment.

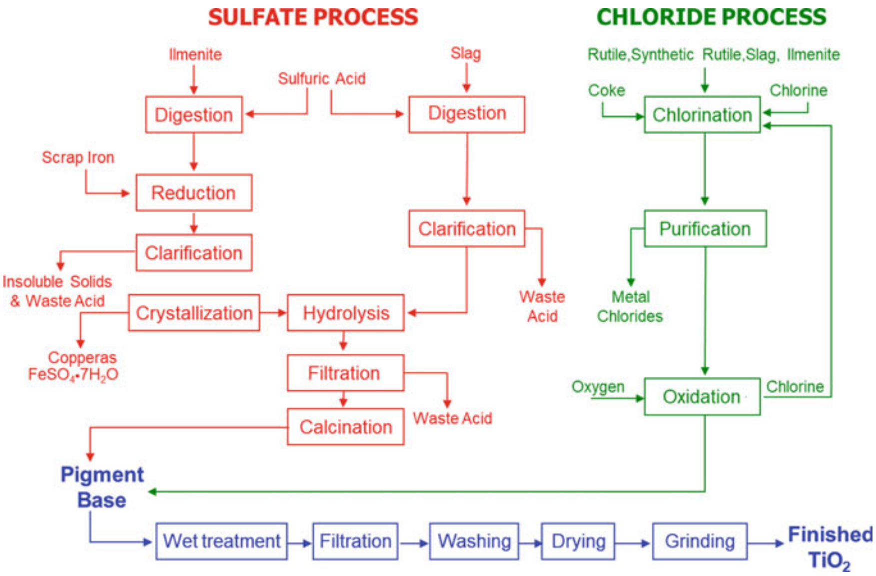

Fig. 7.1 Commercial routes to pigmentary TiO_2

Sulfate Process

In the sulfate process (see Fig. 7.1), the upgraded ore is digested in concentrated sulfuric acid to produce titanyl sulfate. To keep impurities in their more soluble lower oxidation states, reducing conditions are maintained. The titanyl sulfate solution is then purified by first removing the insoluble contaminants and then selectively crystallizing the titanyl sulfate. This material is hydrolyzed and then calcined to produce pigmentary TiO_2 particles. Straight hydrolysis will produce only anatase when calcined, but rutile can be obtained through the addition of rutile seed crystals during the hydrolysis and subsequent calcination steps. The size of the particles is determined by the calcination conditions, and, often, by the incorporation of small amounts of other oxides.

Chloride Process

In the chloride process, the titanium ore is reacted with chlorine gas at high temperatures in the presence of a carbon source. The various minerals present in most ores are oxides, and under these conditions the oxygen content of the oxides is liberated as carbon dioxide while the metal portions are transformed into metal chlorides. Titanium tetrachloride is a liquid under ambient conditions whereas other metal chlorides are typically solids (e.g., ferrous and ferric chlorides) or gases (e.g., aluminum and silicon chlorides). The titanium tetrachloride is purified from these chlorides by fractional distillation and other associated processes.

The purified titanium tetrachloride is then reacted with pre-heated oxygen in a flame reactor, generating pigmentary size TiO_2 particles. The by-product of this reaction, chlorine gas, is recycled to the chlorination reactor. Note that this process does not create a closed loop for the chlorine gas, since the impurities of the chlorination reactor are metal chlorides, which remove a portion of the chlorine from the process.

Property Differences

The main benefits of the sulfate route are that it can generally use a wider range of ores than the chloride route and that it is simpler from a production viewpoint, allowing new producers to enter the market with a relatively simple and unsophisticated process. In addition, both anatase and rutile can be made through this route.

Working against these benefits are the drawbacks that rutile production from the sulfate process can contain anatase impurities, and that non-titanium impurities are more easily removed in the chloride process, generally giving chloride grades a higher brightness than their anatase counterparts. In addition, particle size can be better controlled in the chloride route. The sulfate process also produces high amounts of spent (diluted) sulfuric acid, which must be disposed of or concentrated for recycle in the process. Finally, the chloride route is a continuous process whereas the sulfate route is batch, and so product consistency tends to be better in the chloride route.

Surface Treatment

Once the particles are made, the two process routes converge (Fig. 7.1), and the particles are collected as a water slurry. The next process step is to modify the "raw" particles to optimize performance in specific end-use applications. This is required because the particles in their as-made condition degrade many important properties of paints or plastics, such as opacity, gloss, and durability. This degradation is due to interactions between the particle surface and its surroundings, whether that is water or solvent (a liquid paint), molten resin (plastics during manufacture), or the resin matrix in the final end-use application (paint film, plastic article, or paper laminate). Without modifying the particles in some way, they are generally incompatible with the other ingredients in the paint or plastic.

Since these interactions occur at the particle surface, and since the refractive index of the particle is a bulk, rather than a surface, property, we can modify the pigment surface to improve particle interactions while leaving the most important aspect of the pigment—its light scattering ability—unchanged.[1] This modification is accomplished through the deposition of a material onto the surface, and for this reason most TiO_2 pigment grades are not pure TiO_2. The pigment user should not regard the non-TiO_2 components as impurities—they are quite the opposite. Even though present at only a few percent, these materials greatly improve the value of the pigment and without them it is unlikely that TiO_2 could be used effectively in most applications [2].

In principle, we can deposit any material we wish onto the particle surface. However, if the particle is to maintain many of its important features, we must restrict the characteristics of these surface materials. The important features include colorlessness, non-toxicity, and insolubility in both water and solvents. In addition, these deposited materials, and their precursors, must be easy to handle, relatively inexpensive, and effective at low concentrations so as to limit dilution of the TiO_2 content of the pigment. When we apply these restrictions to the large number of potential particle surface coatings, we arrive at a very short list of practical candidates. This list includes hydrous silica, hydrous alumina, and, at low levels, zirconia. In addition, an organic is often added to the particles near the end of the process (in the grinding stage, discussed in the next section).

The process for depositing these materials is referred to as "surface treatment" or "wet treatment", the latter designation referencing that these treatments are normally deposited onto the pigment when it is a water slurry. The strategy for this deposition is to add a water-soluble precursor of the desired surface coating to a water slurry of the freshly made particles, thoroughly mix the precursor, and then change the slurry conditions (temperature and/or pH) in a way that precipitates the precursor. The exact nature of the change in slurry conditions is important—the same precursor can be precipitated in different ways to alter different properties of the pigment and the end-use materials made from them.

Silica is deposited on the particles using sodium silicate as its precursor. Sodium silicate is a viscous, high pH material that normally contains an excess of NaOH to stabilize against precipitation before use. When the sodium silicate is added to the TiO_2 slurry, the slurry pH increases. The silicate is then neutralized with a strong acid, typically hydrochloric acid or sulfuric acid. During this precipitation the pH remains high because most of the added acid is consumed by the silicate and excess NaOH, rather than remaining in solution and lowering the pH. The pH drops rapidly at the end of the deposition when there is no longer free silicate with which the acid can react.

The silica can be deposited in two forms that differ in the local environment around the individual silicon atoms and in the morphology of the coating. In each case, the silicon atoms are bound to four oxygen atoms, and each oxygen atom is bound to two other atoms. The forms differ in the identity of the second atom bound to the oxygen—it can be a second silicon atom (in which case the oxygen atom bridges two silicon atoms), or it can be a hydrogen atom (in which case the oxygen atom is part of a terminal hydroxide).

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[1] Except by a small reduction due to the slight dilution of the TiO_2 by the surface modifier(s).

The first form of silica is referred to as “dense” silica or “Iler” silica, the latter designation reflecting the first researcher to deposit this form of silica onto TiO_2 [3, 4]. In this form, bridging oxygen atoms dominate, making most of the silicon atoms internal to the structure. This form is typically deposited under high pH and temperature conditions, and with a slow addition of the neutralizing acid [3]. Under these conditions the silicon atoms are more likely to deposit onto existing surfaces (the TiO_2 surface or already-deposited silica), rather than as a separate particle, when they are neutralized. This results in a tight, coherent coating of silica on the TiO_2 surface.

The silica formed in this way deposits as an amorphous material, and as such it has no shape preference (morphology) of its own. Such a coating is desired to mitigate the formation of chemical radicals on the surface of the TiO_2 when exposed to UV light. As will be discussed in Chap. 14, these radicals can leave the surface of the pigment particle and react destructively with the polymer matrix of the paint film or plastic article. Electron micrographs showing this tight, amorphous layer at three magnifications are shown in Fig. 7.2. Because it coats the existing TiO_2 surface, rather than forming new particles (with new surfaces), this form of silica does not change the surface area of the pigment appreciably.

Ideally a single layer of silica would suffice for encapsulating the TiO_2 surface and preventing free radical formation. This would amount to approximately 0.4% SiO_2 by weight. However, in practice, higher levels are required for maximum performance, and grades that contain silica will typically have an amount between 1.5% and 7.5% [5–7]. These higher levels are needed because the silicate moieties deposit randomly on the surface and are just as likely to cover an already covered portion of the surface as they are to cover a uncoated portion of the surface.

The second form of silica has an abundance of Si–OH groups and is referred to as “ionic” silica because these groups deprotonate easily, ionizing the surface of this material. The Si–OH groups are, by their nature, only found at a surface, and because they are predominant in this form of silica, silica deposited in this form has a high surface area and so greatly increases the surface area of the pigment. This form is optimized by precipitating the silica at low temperature, low pH, and quickly [8]. This form of silica is heavily hydrated and so deposits as a thick, porous layer on the particle surface. When used, it is typically present at between 5.0% and 10.0% as SiO_2 by weight, and it greatly increases the surface area of the pigment particles. The raw particles have a surface area of roughly 7–8 m^2/g, while particles treated with ionic silica at these levels have surface areas between 45 and 55 m^2/g.

Because of its appearance under an electron microscope (Fig. 7.3), this form of silica is also called “fluffy” silica. It is used in heavily treated grades made for highly loaded paints, as discussed below.

Alumina, too, can be deposited in two forms, but in this case the local environments around the aluminum atoms are the same (octahedral coordination by bridging oxygen atoms), but the long-range order is different. These forms are pseudo-boehmite, which is crystalline, and amorphous alumina. Each of these forms of alumina provides a different functionality to the pigment.

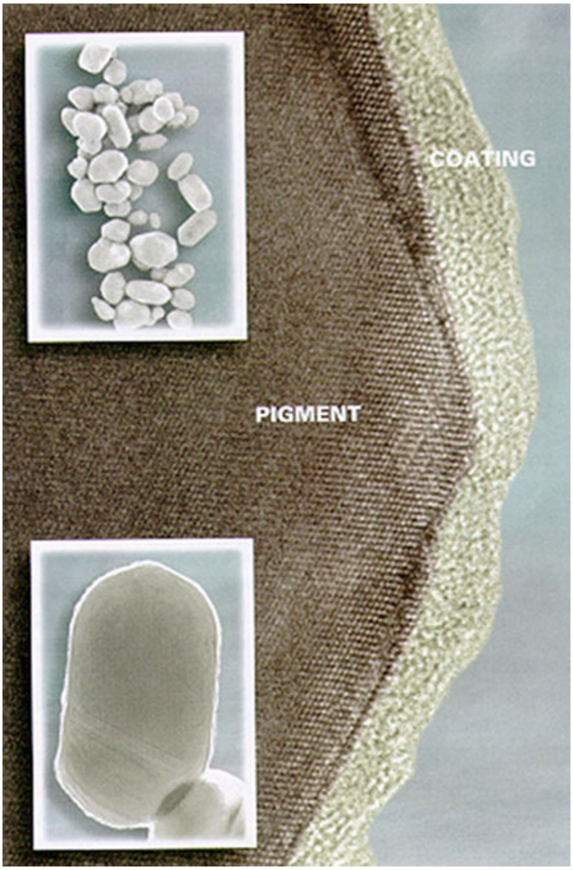

Fig. 7.2 Dense layer of silica on TiO_2 particles at three magnifications. Note the contrast between the lattice fringes of the crystalline TiO_2 core of the particles and the unstructured nature of the amorphous silica surface

The pseudo-boehmite form exists as small (10–20 nm) particles that decorate the particle surface (Fig. 7.4). The function of these particles is to improve the attachment of dispersant molecules onto the pigment surface (see Chap. 11). Although they are present at low amounts (typically 1.5–3.5% measured as Al_2O_3 by weight), they roughly double the pigment surface area to between 15 and 20 m^2/g.

The pseudo-boehmite particles do not entirely coat the surface in the same way as dense silica or amorphous alumina (see below), and so there the surface is still mostly TiO_2. As such it does not improve paint or plastics durability as do the amorphous oxides. This does not decrease their effectiveness, however, at improving pigment dispersion.

The amorphous form of hydrous alumina is similar in morphology and function to the dense form of silica. Its primary role is to increase paint or plastics durability. It has an advantage over silica in that it does not harm the gloss potential of the pigment, as does silica. However, unlike hydrous silica, which is kinetically stable, amorphous alumina can rearrange to the crystalline pseudo-boehmite phase under

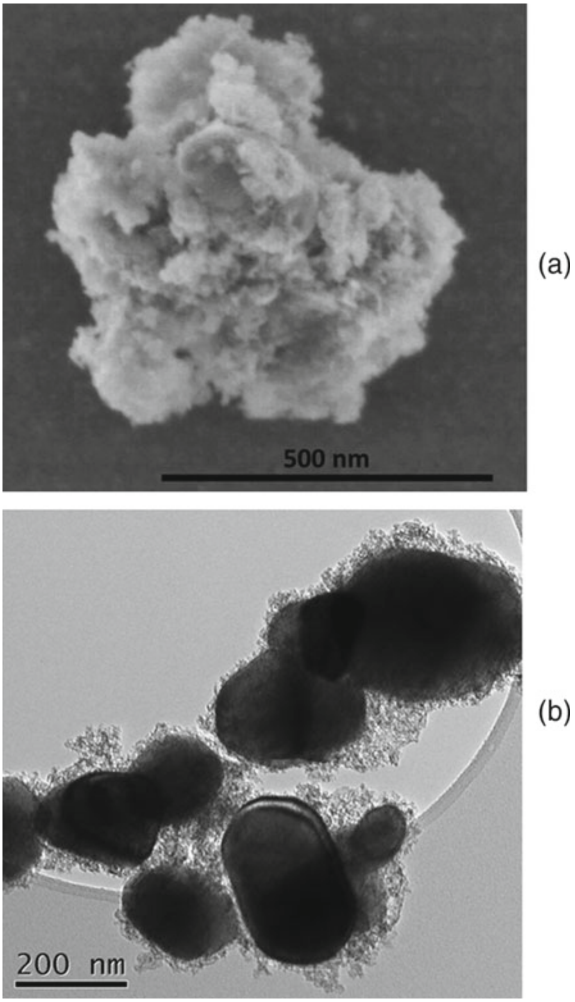

Fig. 7.3 Electron micrographs of ionic silica on TiO_2. **a** SEM. **b** TEM

surface treatment conditions. It is essential that the deposition conditions be closely controlled in order to prevent crystallization. A heteroatom is often incorporated into the amorphous structure in order to stabilize it against crystallization. This atom is most commonly zirconium that is co-precipitated with the alumina [9], although other atoms such as molybdenum, sulfate, phosphate, tin, or fluoride can also be used [10–16].

Fig. 7.4 SEM image of pigmentary TiO_2 coated with pseudo-boehmite particles

Finishing

After surface treatments are complete, the TiO_2 must still be filtered, washed, dried, ground, and packaged or made into a slurry. These last steps are referred to as the finishing process.

In the filter and wash steps, the pigment from wet treatment is dewatered, washed free of soluble impurities, and dried. Several types of filters can be used in this step. Although, for example, filter presses are generally more costly to install and operate, they have the advantage of producing a higher solid discharge that requires less heat to dry. This results in a cost savings and a reduction in CO_2 emissions.

The filter discharge can be dried in a number of oven types. It is important to match the dryer type to the form of the filter discharge. The mass exiting the dryer is then passed through a particle/gas separator which removes the TiO_2 from the gas stream.

A certain degree of particle aggregation is inevitable during TiO_2 production. These agglomerates can be formed during TiO_2 particle formation, during the surface treatment step when touching particles are encapsulated together by the surface treatment agent, and during drying when the surface tension of the water exiting the slurry droplet or cake fragment pulls the particles together. It is therefore necessary to grind the pigment prior to final packaging.

The most effective way to achieve this grind is with a fluid-energy mill (“micronizer”). This type of mill has a disk-shaped chamber (Fig. 7.5). Steam and pigment are tangentially injected into the chamber at supersonic speeds. The clusters of particles collide with the outer wall of the chamber, other particles moving at high speeds, and particles slowed by previous collisions. The centrifugal force generated keeps larger particles towards the outer edge of the fluid-energy mill, and only the desired smaller particles can travel to the center where the steam is discharged. The pigment/steam mix is then separated in a bag house or cyclone. The exiting steam can be used in other aspects of the process. Note that this process separates touching particles, but it does not actually grind the individual particles into smaller sizes.

A uniform particle flow is required for the particles to grind with optimal efficiency. Organic “grind aids” can be applied to the pigment surface prior to injection into the fluid-energy mill to facilitate a uniform flow. These aids are typically low weight, high functionality organic molecules. In addition, organic hydrophobic materials can be applied to enhance dispersibility of the TiO_2 pigment in plastics applications [17].

While fluid-energy mills are effective for pigment grinding, they also require high energies. Because of this the pigment is often pre-ground in the slurry state with media, sand, or ball mills earlier in the process (either before or after surface treatment). This reduces the very large agglomerates into smaller clusters that are more efficiently ground in a fluid-energy mill to achieve primary particle sizes.

Finally, the resulting powder is either packaged in bags (typically 25 kg), semi-bulk containers (½ or full metric ton sacks), or bulk containers (20–40 metric tons) destined for silo storage. The pigment may also be made into a water slurry ready for incorporation into a latex paint. This has the advantage that it allows the paint manufacturer to skip a step in the paint making process, and also allows for a more exact metering of the pigment into the paint batch (that is, the minimum increment of pigment added is less than for dry material). However, care is required to assure

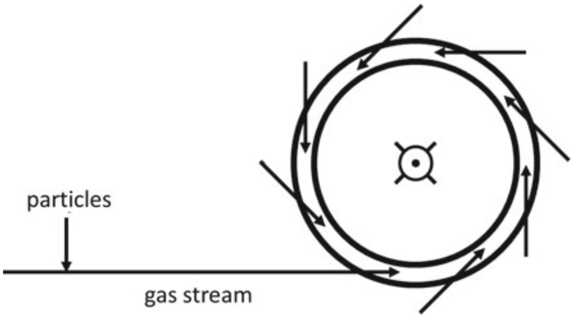

Fig. 7.5 Overhead view of a fluid-energy mill. Gas exits out of the page at the center of the chamber

that the slurry remains stable for extended periods of time, and the slurry must be actively acted on during storage to reduce settling.

Pigment Design

A wide assortment of TiO_2 pigment grades is available for use in the coatings, plastics, and paper laminate industries. Each grade is customized with a specific application in mind. For example, grades are available that optimize paint gloss, durability, processibility, electrical resistance, and so on. Similarly, grades are available for plastics that are optimized for processibility, durability, and color properties (e.g., undertone).

In general, we can divide most TiO_2 pigment grades into one of two categories: those for specific applications (e.g., superdurable paints, electrodeposition coatings, etc.) and those that are meant to satisfy the needs of multiple paint or plastics types. The latter are referred to as "universal" or "multipurpose" grades, and their value to the paint or plastics manufacturer is raw material rationalization—by using a universal grade, a single pigment can be inventoried, rather than a separate pigment for each paint or plastic type.

TiO_2 pigment grades typically differ in two ways: the exact particle size distribution (in particular, the mean size) and the surface treatment (the identity, amounts, and deposition conditions for the surface coatings). The former determines the undertone of the pigment—blue or neutral. In regard to the latter, it is remarkable that so many different product properties can be altered and optimized by using only a few surface treatment materials. This reflects the ingenuity and creativity of TiO_2 product developers in making the most out of limited materials available to them.

Particle Size

The importance of TiO_2 particle size to light scattering strength was discussed in Chap. 3. There we saw that the optimal particle diameter for TiO_2 to scatter visible light is roughly 0.25 microns. We also saw, in Chap. 4, that the exact optimal size depends on the concentration of the particles in the polymer matrix. We can divide these concentrations into two categories—low concentrations (typically less than 1% by volume) in plastics and high concentrations (typically between 8 and 20% by volume) in coatings. The optimal particle size at low concentrations is roughly 0.23 microns while that at the higher concentrations is roughly 0.26 microns.

Control of size over such a small range can be a challenge to the pigment producer. However, those producers with a long history of manufacture have generally optimized their processes to allow for such fine particle control. Although differentiating grades by the typical particle size measurement techniques is difficult (see Chap. 2), differences can be detected by eye. The smaller particles preferentially scatter blue light while the larger particles scatter all wavelengths more evenly. As a result, a mixture of the TiO_2 particles of interest with a black pigment (generally carbon black or black iron oxide) will have a blue undertone for grades destined for plastic and a more neutral undertone for those destined for coatings.

Durability

The term “durable” is often used in connection with a particular grade of TiO_2 pigment. This term describes the effect of the TiO_2 on the outdoor durability of the paint or plastic into which it is incorporated, rather than the durability of the TiO_2 pigment itself. Unlike the organic matrices of paints and plastics, TiO_2 and the oxides used to coat its surfaces are fully oxidized and so do not react with oxygen from the air.

As described above, pigment grades are made durable by the application of an amorphous coating that completely separates the TiO_2 surface from its surroundings. This enhances paint and plastic durabilities because the TiO_2 surface becomes reactive when irradiated by UV light. Details of this reactivity are described in Chap. 14.

Surface-deposited silica gives a higher durability than amorphous alumina [18], and a combination of the two gives better durability than either alone [6, 7]. However, silica-coated TiO_2 has traditionally been viewed as difficult to disperse and an inhibitor of high gloss in paint applications. For this reason, many durable grades of TiO_2 are based on amorphous alumina coatings rather than silica coatings.

There is an additional consideration regarding the use of hydrous oxides to improve the durability of a plastic. The temperatures in certain plastics processing steps can be high enough to drive a significant portion of the waters of hydration out of these pigments. This causes gas bubble to form, which, in thin film applications, leads to thin spots or holes. This process is referred to as lacing. Alternative coatings that contain fewer waters of hydration (and so do not lace) yet still provide a beneficial effect on durability have been reported [14, 19].

Dispersibility

The dispersion of particles into a liquid paint is covered in detail in Chap. 11 and into a molten polymer in Chap. 12. There are specific considerations for optimizing TiO_2 dispersion in both paint and plastic processing. Ideally these particles would disperse quickly and with minimal energy. In the case of paints, the dispersion must remain stable for extended periods of time.

The ease of dispersion can be controlled using suitable surface modifications. For coating grades of TiO_2, this consists mainly of depositing the proper form of alumina as the outermost pigment surface layer. Doing so not only improves the wettability of the TiO_2 pigment, which can be a slow step in dispersion, but can also improve dispersion stability by supplying a surface to which dispersant molecules attach strongly and permanently. In addition, certain additives present during the alumina precipitation can enhance the dispersibility of the pigment in water [7, 8].

Pigment dispersion in plastics can be improved by making the pigment surface hydrophobic (lipophilic). The hydrous oxide surfaces of TiO_2 pigment are hydrophilic and as such are incompatible with the molten polymer into which it is incorporated, making dispersion difficult. This issue can be reduced significantly by adding an appropriate surface agent during the final stages of pigment finishing [20]. This also has the advantage of reducing the amount of surface water adsorbed on the pigment, and thus reducing the possibility of lacing.

Gloss

The gloss of a paint film is the visual impression given from the light reflected at the film surface. It is determined by the quantity of the light that is specularly reflected from a surface (i.e., reflected at the mirror angle) [19]. As such it is a function of the surface smoothness at the optical scale (0.5 microns and above).

Surface smoothness is affected by a number of factors. Obviously, a major factor is the size of the particles in the paint or plastic. Extender particles are generally very large compared to the wavelength of visible light, and as such their presence will typically decrease gloss. This occurs by near-surface particles perturbing the surface resin, that is, the particles themselves do not protrude through the surface, but nonetheless have an effect on it.

Although near-surface TiO_2 particles will also affect the surface smoothness, when the particles are in an individual and separated state, the surface perturbations are too small to impact gloss. However, groups of particles (agglomerates of flocculates) are large enough to affect gloss (Fig. 7.6). This effect can be seen, as an example, by

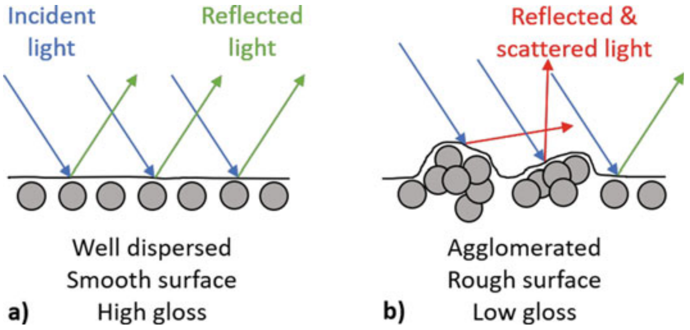

Fig. 7.6 Comparison of the impact of agglomeration and surface roughness of two paint films on gloss

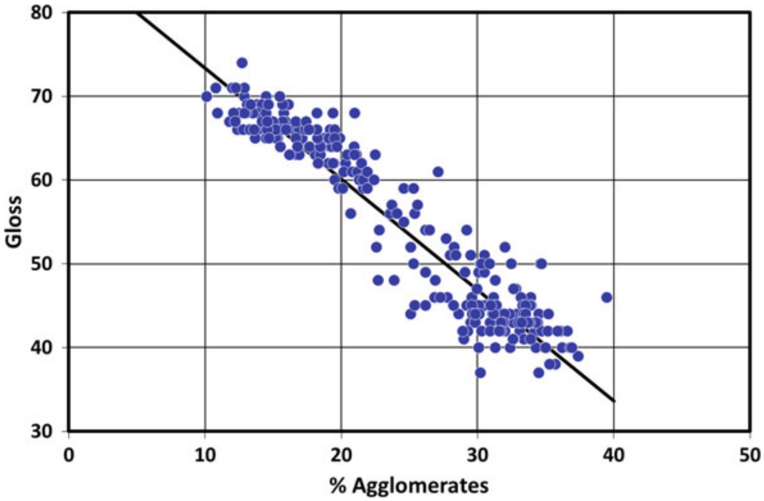

Fig. 7.7 Effect of number of TiO_2 agglomerates on the gloss of a standard emulsion paint

comparing the gloss of a standard emulsion paint made with different TiO_2 samples as a function of the percent of particle agglomerates in those samples (Fig. 7.7).

As mentioned above, not all grades of TiO_2 give the same degree of gloss. This can be attributed to three factors. The first is the degree to which the particles maintain their separate identities as they are formed. In both the sulfate and the chloride processes, particle formation takes place at relatively high temperatures. In the sulfate process, this is during the calcination step, and in the chloride process the reaction of $TiCl_4$ with oxygen occurs in a flame reactor. Small particles become sticky at high temperatures and are prone to attaching to one another. For this reason, the exact conditions of the calcination or flame reaction, in particular, the time at temperature and the cooling rate, affect the number of agglomerates in the final product.

The second factor that affects the relationship between TiO_2 grade and gloss is the nature of the oxides deposited in the surface treatment step. In particular, the silica that is deposited to increase the durability of the paints or plastics into which a TiO_2 pigment is incorporated has a deleterious effect on gloss. In some cases, this issue can be overcome by replacing one oxide with another, although this can cause negative effects on other important end-use properties.

Finally, grind intensity affects gloss. This applies to both the grinding that is done both in the fluid-energy mill at the final stages of pigment production and during incorporation of the pigment into paints or plastics. An example of the latter is shown in Fig. 7.8. Here we show the development of distinctness of image (one form of gloss) as a function of grind time in a paint.

In general, the gloss of a paint can be readily decreased by adding a flatting agent, but it is not possible to add a material that will increase the gloss of a paint. Because of this, universal or multipurpose grades of TiO_2 pigment will typically have a high gloss potential.

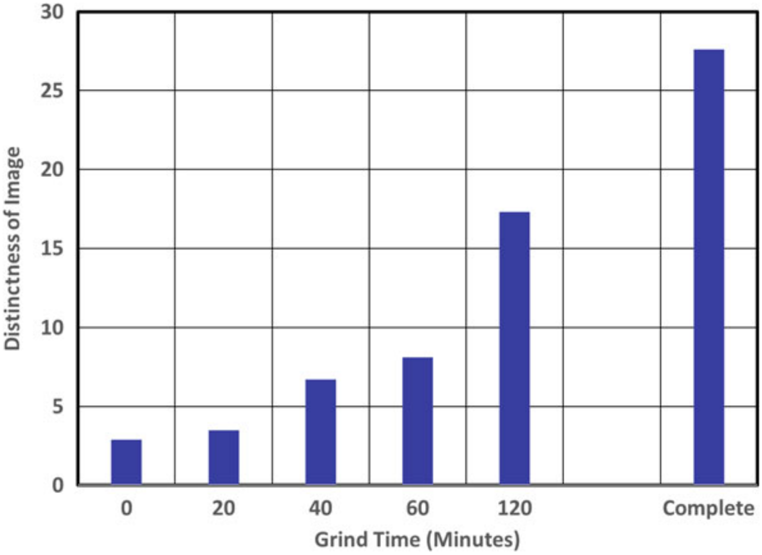

Fig. 7.8 Evolution of distinctness of image during high shear dispersion TiO_2 paint grind. Complete dispersion was achieved by subsequent media milling

Opacity

The light scattering ability of TiO_2 is determined by two factors: particle size and degree of particle dispersion. In Chap. 3, we saw the importance of particle size to light scattering strength. Light scattering is optimized when the particles are roughly 0.25 microns. However, as discussed in Chap. 4, there are slight differences in the optimal size based on the concentration of the particles in the polymer matrix. At the low concentrations, typical of plastics applications, slightly smaller particles are the most efficient. At the higher concentrations seen in paints, slightly larger particles are optimal.

In Chap. 4, we also saw the importance of dispersion on light scattering. Particles that are close together interfere with one another's ability to scatter light due to scattering volume overlap. As a result, good dispersion of the TiO_2 particles in the paint or plastic is necessary for their optimal efficiency, in the same way that good dispersion is necessary for high paint gloss. Chapters 11 and 12 describe the dispersion processes, and how they are optimized, for particles incorporated into paints and plastics, respectively.

Highly Treated Grades

As described earlier, TiO_2 pigment grades tend to fall into the categories of those optimized for a specific end-use and those intended for multiple end-uses. Perhaps the most important of the grades optimized for a specific end-use are the highly treated pigments used in highly crowded paint systems. These paints contain high concentrations of extender, which are typically present as a mix of large and small particles. In these paints, there is not enough resin to fill the inter-particle regions, and so these regions are partially occupied with air. The effect of these air voids on opacity will be discussed later.

Highly treated grades are preferred in these highly crowded paint systems because the TiO_2 particles, which are crowded into the interstitial regions between the larger extender particles, are spaced farther apart than universal TiO_2 pigment in these regions. Because of dilution by the thick, porous coating, there are fewer highly treated particles in these regions than there would be an equal weight of universal TiO_2, but the scattering increase due to better particle spacing more than offsets decrease due to fewer TiO_2 particles per unit weight of pigment. This gives crowded paints made with the highly treated particles better opacity than those with the universal particles, as was discussed in depth in Chap. 4.

Alternative White Pigments

Because of its unmatched refractive index, titanium dioxide is the preeminent white pigment used in the coatings, plastics, and paper laminate industries. However, other white pigments are sometimes used in these industries, particularly in niche applications where TiO_2 brings an unwanted property. As an example, TiO_2 particles scratch the reinforcing glass fibers used in certain plastics applications, causing them to break during processing. Here a less abrasive white pigment must be used, despite the loss of opacity. Another example is the continued use of some older pigments due to the cost or lack of availability of TiO_2.

Alternative Particles

Particulate alternatives to TiO_2 pigments include zinc oxide, zinc sulfide, and lithopone. In the past, oxides of lead and antimony have been used for this purpose, but due to their toxicity and expense,[2] these pigments have all but disappeared from use. The relative opacities of these materials, as reported by Stieg [21], are given in Table 7.1. These values underscore the vast hiding power advantage that TiO_2 enjoys over its alternatives.

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[2] This refers to expense on a coverage basis—that is, based on the cost to make a unit area of paint film or plastic opaque—rather than on a weight basis.

Table 7.1 Relative hiding strengths of white pigments in paints [21]

Material	Relative opacity
Titanium dioxide	100.0
Zinc sulfide	50.4
Lithopone	23.5
Zinc oxide	17.4
Carbonate white lead	13.0
Basic lead sulfate	11.3

Zinc oxide had been used extensively in the Southern USA and other regions having persistent high humidity because it is a mildewstat. It achieves this property through its slight solubility in water—dissolved zinc ions discourage the growth of mildew and fungus. The use of zinc oxide in paints has mostly disappeared because it is an aquatic toxin. This is directly linked to its mildewstatic properties—while it is desirable for it to be toxic to micro-organisms on a painted surface, it is undesirable for it to be toxic to micro-organisms in a river or lake. It is still sometimes used at low levels as a bactericide for the liquid paint during storage.

Zinc sulfide is sometimes used by itself in paint primers, where it can indicate where the paint has been applied without the need to completely hide the substrate [22]. In addition, it has high thermal conductivity (which helps paints and plastics stay cool), lower UV absorption (an advantage in UV-cured paints and applications using optical brighteners), low abrasivity (making it preferred in glass fiber reinforced plastics and in situations where metal marking during plastics production is an issue), and is relatively easy to disperse in plastics.

Zinc sulfide is more commonly used as lithopone, which is an equal molar mix of zinc sulfide and barium sulfate (28% ZnS and 72% $BaSO_4$ on a weight basis). This material is conveniently made by mixing zinc sulfate and barium sulfide in water. Both of these materials dissolve in water, but their reaction products do not. Pure lithopone was substantially replaced by TiO_2 in the mid part of the last century. As a point of comparison, the current annual market for lithopone, on a monetary basis, is about 1% that of titanium dioxide. Modified lithopone, which was fortified with an excess of zinc sulfide or with titanium dioxide, enjoyed a brief popularity during the transition from lithophone to titanium dioxide [21]. Roughly three-quarters of current lithopone production goes into the coatings market, where it is still used in some applications due to its low cost, its ability to protect the paint from UV light (although the ZnS component of lithopone can discolor on UV exposure), and its fungicidal properties. It is used in the plastics industry when lacing (water vapor release during plastic film processing) would otherwise be an issue.

Entrained Air

In addition to the materials described above, air can be used as a TiO_2 alternative for white opacity. This is because the refractive index of air is different from that of resin—in this case, lower than the resin matrix, rather than higher, as is the case with the materials described above. In order to scatter light effectively, air must be present in the form of discrete voids (bubbles) or pores (networks of joined pores). The functional difference between these forms is that pores allow for the ready transport of liquids and gases through the polymer matrix while discrete air units do not. In addition, because pores are larger than individual voids, they weaken the polymer to a greater extent than voids. These two forms of air also differ in the way they are created.

Discrete voids can be created in a number of ways. In certain plastics, such as polystyrene, a blowing agent can be added to the molten polymer [23]. This agent is a material that volatilizes at process temperatures, either through decomposition or boiling, and releases gas bubbles that are then trapped within the polymer when it solidifies. Alternatively, an inert gas can be dissolved in the molten resin under pressure. When the pressure is released, for example, by letting the mixture down to atmospheric pressure, bubbles are formed.

An excellent example of this form of air void is expanded polystyrene (EPS), a material familiar to many by the brand name “Styrofoam®”. EPS is typically bright white but contains no white pigments. Instead light is scattered from a multitude of voids within the polymer. The voids in EPS materials are created by vaporizing small pockets of pentane that are incorporated into molten resin.

Air pockets in plastic films can also be formed through cavitation [24, 25]. In this process, small particles, often calcium carbonate, are incorporated into a plastic film, and then the film stretched. When the adhesive strength at the polymer/particle interfaces is low, stretching the film pulls the polymer away from the particles, creating elongated voids with a particle at the center.

The waterborne coatings industry also incorporates air voids into paint films. One way of doing this is by the use of hollow sphere opaque particles or HSOPs (these are also discussed in Chaps. 10 and 16) [26–28]. These are individual spherical polymer shells with an empty center. In the liquid paint, the center is filled with water, but in the dry film it is filled with air. These particles are formed by encapsulating a swellable polymer sphere with a rigid polymer that has an accessible softening point. The internal polymer is swelled at a temperature where the outer polymer is soft. The temperature is then lowered to make the shell rigid, and then the internal polymer is de-swelled to create a void.

Due to the limited difference in refractive index between air and resin, these particles allow for only a partial replacement of TiO_2, and only in paints for which the TiO_2 pigment volume concentration (PVC) is close to 20. Although the use of HSOPs is currently restricted to paints and limited paper laminate applications, research is currently underway to apply this technology to plastics [29].

Flash calcined clay particles are an alternative means by which encapsulated air can be brought into a paint film. Clay is a mineral composed of alternating layers of silica and alumina that are joined together by waters of hydration (see Chap. 9). When clay particles are rapidly heated, their outer surfaces quickly become glassy, sealing the interior of the particle. The interstitial water molecules then vaporize, resulting in the formation of internal, sealed voids.

As mentioned in the section on highly treated grades of TiO_2, a different type of air scattering is commonly used to opacify flat architectural (décor) paints. Here the paint is formulated with a high content of particles—mostly extender particles, but lesser amounts of pigmentary particles are typical—and a low content of resin. The balance between particle and resin volumes is so great that there is not enough resin to completely fill the voids between the particles. Instead much of the inter-particle voids are filled by air. We refer to such paints as being formulated above CPVC, a subject that is discussed in depth in Chaps. 4 and 16.

The air regions formed in this way are fundamentally different than those described above—those described above are discrete, self-contained voids or bubbles while the voids found in paints formulated above their CPVC join together into an extensive network of pores. This has implications on the strength, protectiveness, and stainability of paints employing this strategy.

Many older technologies, which included pigment composites and various ways of incorporating air into a paint or plastic [21], are no longer in use [30].

Summary

Titanium dioxide pigments are the highest volume pigment used in the paint and plastic industries. This is because of its high whiteness, brightness, and opacifying abilities. Most paints, even those that are not white, contain TiO_2 as an opacifying agent, often in high amounts.

The opacity of pigmentary TiO_2 has two origins. The first is its high refractive index, which maximizes scattering on a volume basis (refer to Chap. 3). The second is the TiO_2 industry's ability to tightly control the TiO_2 particle size, as well as modify the particle surfaces in order to enhance other end-use properties.

There are two processes to form the individual TiO_2 particles. In each process, the titanium containing ore is reacted to liberate the titanium content. In one case, this is done with sulfuric acid, to make titanyl sulfate, and in the other with chlorine gas to make titanium tetrachloride. In both cases, the titanium containing compound is separated from impurities, and then reacted to form TiO_2. Process conditions are critical for achieving the correct particle size.

Regardless of how the individual particles are made, they are then surface modified to improve the interactions between the particles and the other components of the paint or plastic. These modifications consist of the precipitation of hydrous alumina and/or silica under carefully controlled conditions so as the surface agent precipitates in the proper form. In some cases, a third metal oxide, such as zirconia, is co-precipitated with the alumina. Finally, a thin organic coating is often placed on the particles immediately before they are ground.

The size of the TiO_2 particle determines its undertone. The optimal particle size is dependent on the concentration of the TiO_2 pigment in the end-use application. Applications with low TiO_2 concentrations, such as most plastics, benefit from slightly smaller particles, and applications with relatively high TiO_2 content, such as paints, benefit from slightly larger particles.

The surface treatments applied to the particles affect the dispersibility of the pigment as well as the gloss, opacity, and durability of the paint or plastic into which it is incorporated. In general, good dispersion is desired as this optimizes opacity and allows for a high paint gloss. This is desired even in paints with mid-to-low gloss because the high gloss grades of TiO_2 can be used in these paints, and a flatting agent can be added to reduce gloss to the desired level. As such the TiO_2 grades can go into multiple paint applications, earning them the designation of "universal" TiO_2 pigment.

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