

SOURCES OF FILLERS, THEIR CHEMICAL COMPOSITION, PROPERTIES, AND MORPHOLOGY

The information included in this chapter is based on the data selected from the technical information included in the manufacturers literature and research papers. The main goal of this chapter is to provide information on:

- Physical and chemical characteristics of fillers
- Morphology of filler particles
- Sources of fillers
- Manufacturers
- Important commercial grades
- Major applications
- Relevant studies

Data for each filler are presented in the form of a standard table which contains, for a particular filler, only sections for which information was available. The physical characteristics of fillers and other data on characteristic parameters are taken from the manufacturers literature and open literature to show the range of properties rather than values for a particular grade. The information on the characteristics of every grade is extensive and comes from over 150 manufacturers. Large quantity of information gathered is presented as established data in tabular form. A future publication on CD-ROM will present full information on all grades available worldwide.

Commercial information is presented in an abbreviated form in the individual tables. In addition to this information, there is an appendix included at the end of this book which provides references to the manufacturers and distributors of these products worldwide. There is no distinction made in the tables between the manufacturers and distributors.

The text which follows the table for a particular group of fillers discusses manufacturing methods, morphology and explains and amplifies the tabular data.

2.1 PARTICULATE FILLERS

2.1.1 ALUMINUM FLAKES AND POWDER¹⁻⁶

Names: aluminum flakes, aluminum pigments, leafing aluminum pigments		CAS #: 7429-90-5
Chemical formula: Al		Functionality: OH
Chemical composition: Al - 95.3-99.97%; oxide content - 1-3%, lubricant content - 0.2-4%		
Trace elements: Si - 0.05-.025%, Fe - 0.1-0.4%, other - 0.03-0.05%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.7	Mohs hardness: 2-2.9	Melting point, °C: 660
Specific heat, kJ/kg · K: 0.90		
Thermal conductivity, W/K · m: 204		Thermal expansion coefficient, 1/K: 25x10 ⁻⁶
CHEMICAL PROPERTIES		
Chemical resistance: excellent corrosion resistance, reacts with alkaline and acidic solutions yielding hydrogen gas		
OPTICAL & ELECTRICAL PROPERTIES		
Color: silvery white to chromelike (leafing) metalescent (nonleafing)		
Resistivity, Ω-cm: 2.8 x 10 ⁻⁶		
MORPHOLOGY		
Particle shape: flat, spherical	Crystal structure: cubic	Particle size, μm: 10-23 (powder)
Aspect ratio: 20-100	Particle thickness, μm: 0.1-2	Particle length, μm: 0.5-200
Sieve analysis: 0.1-20% retained on 325 (44 μm) sieve		Specific surface area, m ² /g: 5-35
MANUFACTURER & BRAND NAMES: Silberline Manufacturing Co., Inc., Tamaqua, PA, USA manufactures several hundred grades of aluminum powders and flakes. The products are grouped by the particle character (powder, leafing, nonleafing), resistance to acids (non-resistant, resistant), application (general, waterborne, plastics, printing inks, specialty, other (inhibited aluminum pigments, water dispersible aluminum pigments, degradation resistant, sparkle and high series, lenticular series, glitter series, black iron flake, spherical pigments, extra sparkle spheres, metalescent pigments, dedusted flake, colored pigments, resin treated grades)). The following are trade names: Aqua Paste, Aquasil, Aquavex, EternaBrite, Extra Fine, Hydro Paste, Lansford, SilBerCotes, SilBerTones, Silcroma, Sil-O-Wet, Silvar, Silvet, Silvex, Sparkle Silver, Stamford, Super Fine, Tufflake Transmet, Columbus, OH, USA Aluminum, copper, brass, and zinc particulate materials manufactured in various shapes of square flake (K-102), rectangular flake (K-101), flat fiber (K-107), flake (K-109), needle (N-101), and tadpole (T-101, T-102, T-103). The symbols in parentheses are the grades numbers for aluminum. If other metal is requested the grade number is derived from the metal number which is the first digit (1 - aluminum, 2 - copper, 3 - zinc, 4 - brass). For example, square flake from brass is K-402. The materials are manufactured by two technologies Melt spin and Spinning cup which are discussed below.		

MAJOR PRODUCT APPLICATIONS: coatings, inks, roofing, plastics, automotive, powder coatings, containers for sterilizing and storing medical instruments, molding tools, heat sinks for electronic devices, time-delay switch, egg poachers
MAJOR ADVANTAGES: heat reflectivity, low emissivity, temperature resistance, moisture and oxygen barrier properties, sealing properties, reinforcement

The technology of production of aluminum powders and flakes dates back to 1930 when a safe process of manufacture was developed by Hall of Columbia University. This method is still used today for most manufactured pigments. The principle of manufacture is based on wet ball milling aluminum in the presence of a lubricant and mineral spirits.

The grinding process depends on the grade to be manufactured and usually takes 5-40 hours. The grade is determined by the particle size and grading is accomplished by filtering the slurry to remove large flakes. Typical leafing grades have 55-65% leafing flakes. The ultraleafing grades have almost 100% leafing flakes. An important difference exists between leafing and nonleafing flakes. Leaving flakes are obtained by the addition of a fatty acid (e.g., stearic acid) lubricant during the milling process. The lubricant coats the surface of flakes which become hydrophobic. There is a large difference in behavior between leafing and nonleafing flakes in coatings. Nonleafing flakes are uniformly distributed through the thickness of coating. They are preferentially oriented parallel to surface but this orientation is not perfect. Leafing flakes are mostly situated close to the paint surface and far from the substrate. Their orientation is much closer to parallel than the orientation of nonleafing flakes. Nonleafing pigments are frequently used with other pigments to obtain colored metallic finish. Leafing flakes give paints a metallic luster and reflectivity. In plastics, a true leafing effect has not yet been accomplished.

Processing of materials containing aluminum flakes must take into account their fragile nature. If flakes are exposed to extensive shearing forces they will degrade. Slow mixing and gradual dilution of flakes normally produces good results.

The commercial products are in most cases in the form of a paste. Standard pastes contain 27-35% mineral spirits. For waterborne applications carrier contains mixture of mineral spirits, nitroethane, and polypropylene glycol. Ink grades contain isopropyl alcohol or ink oil. Plastic grades are dispersed in plasticizer (DOP, DIDP), mineral oil or resin.

Transmet Corporation manufactures flakes by a Rapid Solidification Technology. There are two variations of this method: Melt spin and Spinning cup methods. In the Melt spin method, molten metal of any composition (pure metal or alloy) is driven through an orifice and the shape formed in the orifice (continuous sheet) is rapidly cooled on a chilling block. This metal sheet is cut into segments in the form of flakes (square and rectangular), flat fibers, and ribbons of desired

dimensions. Typically, the sheet has thickness of $25\text{ }\mu\text{m}$ and the cut sides (length or width) have a length in the range of 0.5 to 2 mm. In the Spinning cup method, molten metal is driven through an orifice onto a rotating element (spinning cup) which works in manner similar to spray drying equipment. The particles are dispersed in space by tangential forces. In this process, spheres, needles and tadpoles are manufactured. The method can produce a broad range of compositions and shapes. It was determined, based on the rates of chemical reactions, that the shape of particles has a pronounced effect on the reaction rate. The shape of particles and their composition has an effect on their performance in conductive plastics and as reflecting media in coatings. The metal particles produced by this method have found applications in various products which are required to conduct heat and electricity, to shield EMI, and to reflect radiation in roofing materials, in addition to the traditional use of such materials in chemical and metallurgical processes. Figure 19.17 shows the cost of EMI shielding using aluminum flakes in comparison with other materials based on Transmet estimation.

2.1.2 ALUMINUM BORATE WHISKERS⁷⁻⁸

Name: aluminum borate whisker		
Chemical formula: $(Al_2O_3)_9(B_2O_3)_2$		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.93	Thermal expansion coefficient: 7.4×10^{-6}	
Tensile strength, GPa: 7.8	Tensile modulus, GPa: 400	Compressive strength, GPa: 3.9
MORPHOLOGY		
Particle shape: ribbon or cylinder	Crystal structure: single crystal	Specific surface area, m ² /g: 2.5
Particle length, μm: 10-30	Particle diameter, μm: 0.5-1	Aspect ratio: 20-30
MANUFACTURER & BRAND NAME: Shikoku Chemical Corp. - Alborex G		
MAJOR PRODUCT APPLICATIONS: experimental phase as reinforcing filler		

2.1.3 ALUMINUM OXIDE⁹⁻¹²

Names: anhydrous aluminum oxide, α-, or γ-, or θ-alumina		CAS #: 1344-28-1
Chemical formula: Al ₂ O ₃		Functionality: PBD-coated ¹⁰
Chemical composition: Al ₂ O ₃ - 99.6%		
Trace elements: SiO ₂ - 0.02-0.1%, Fe ₂ O ₃ - 0.03-0.2%, TiO ₂ - 0.1%, Na ₂ O - 0.04-5%, HCl - < 0.5%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 3.4-3.9	Mohs hardness: 9	Melting point, °C: 2015-2072
Thermal conductivity, W/K · m: 20.5-29.3	Maximum temperature of use, °C: 1600	
Compressive strength, MPa: 2000	Surface properties: hydrophilic	
CHEMICAL PROPERTIES		
Moisture content, %: 4-5	Adsorbed moisture, %: 17-27%	pH of water suspension: 8-10
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 1.7	Whiteness: 80-90	
Color: white through off white to brown	Volume resistivity, Ω-cm: >10 ¹⁴	
Dielectric constant: 9-9.5	Dielectric strength, V/cm: 2560	Loss tangent: 0.0002-0.004
MORPHOLOGY		
Particle shape: spherical or irregular	Pore diameter, Å: 58-240	
Particle size, nm: 13-105	Crystal structure: rhombic	Oil absorption, g/100 g: 25-225
Sieve analysis: 0.05-5% on 45 μm sieve	Spec. surface area, m ² /g: 0.3-325	
MANUFACTURERS & BRAND NAMES: Alcan Chemicals, Gerrards Cross, UK Milled grades RMA, MA, MAFR Calcinated alumina C-70 series, RA (ceramics), Cera (polishing, electrical components), CA, CG, CK (glass, ceramic fibers, etc), Baco (polishing), MA-LS (refractories, ceramics), LS (electrical and engineering components) Activated alumina AA (catalysts, desiccant, fluorine removal from water), Acidsorb (adsorption of HCl from chemical processes), Actibond (refractory binder) Biotage, Inc. Unisphere Degussa AG, Frankfurt/Main, Germany Al ₂ O ₃ C Electro Abrasives Corporation, Buffalo, NY, USA Electro-Ox brown aluminum oxide and precision aluminum oxide abrasive Morgan Matroc, Stourport-on-Seven, UK Aluminum oxide Nanophase Technologies Corporation, Burr Ridge, IL, USA NanoTec Aluminum Oxide The PQ Corporation, Valley Forge, PA, USA Nyacol Colloidal Alumina, Nyacol AL20SD		
MAJOR PRODUCT APPLICATIONS: composites, ceramics, refractories, abrasives, copy toner, electro-optic devices, polishing, electrical and engineering components, acid adsorption, catalyst, nanocomposites		

Refractory grades have large particle sizes in the range of 5-25 μm and very low surface area at 0.3-1 m^2/g . Their specific gravity is high at 3.95 g/cm^3 . Calcinated alumina is produced by the Bayer calcination process from aluminum trihydroxide in rotary kilns. During the process, water is removed and stable α -alumina structure is obtained. The particle size of calcinated grades is similar to refractory grades unless they are milled. Smaller particle size grades have a specific surface area of 3-10 m^2/g . Activated aluminas have particle sizes in the range of 6-80 μm but very large specific surface areas in the range of 220-325 m^2/g . They can readily absorb water to equilibrium at 18-22%.

The grades produced by Nanophase Technologies Corporation are obtained in a synthetic way by evaporation of the metal and its subsequent oxidation. This process produces regular spherical particles as shown in Figure 2.1.¹³⁻¹⁴ These materials have properties which cannot be duplicated by conventional grades of alumina obtained from minerals or by chemical synthesis. The nanoparticles are known to enhance mechanical performance of plastic materials (tensile, hardness, wear, etc.). The hardness of compressed ceramics increases as the particle size decreases and it is possible to obtain materials which allow considerable light transmission. These materials are on the market now and they will find many high technology applications.

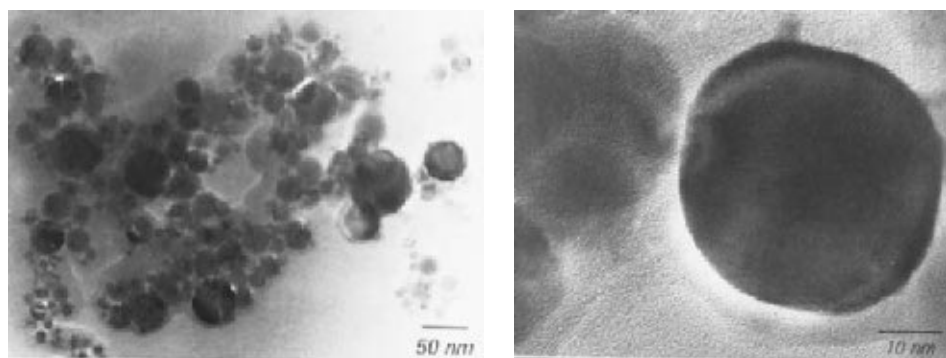


Figure 2.1. TEM of NanoTek aluminum oxide. *Courtesy of Nanophase Technologies Corporation, Burr Ridge, IL, USA.*

2.1.4 ALUMINUM TRIHYDROXIDE¹⁵⁻³⁹

Names: aluminum trihydroxide, aluminum hydroxide, hydrated alumina		CAS #: 21645-51-2
Chemical formula: Al(OH) ₃ or Al ₂ O ₃ ·3H ₂ O		Functionality: OH, methacryl, vinyl, stearic acid, viscosity reducer (Alcan grades S)
Chemical composition: Al(OH) ₃ - 94-97%, Fe ₂ O ₃ - 0.01%, SiO ₂ - 0.01-0.03%, Na ₂ O - 0.2-0.5%		
Trace elements: Pb < 0.0005%, As < 0.0002%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.4	Mohs hardness: 2.5-3.5	Melting point, °C: 290 (decomp)
Loss on ignition, %: 34.5		
CHEMICAL PROPERTIES		
Chemical resistance: amphoteric material		
Moisture content, %: 0.1-0.7		
pH of water suspension: 8-10.5	Loss on ignition, %: 34.6%	Specific conductivity, μS/cm: 70
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 1.57-1.59	Reflectance: 89-95	Whiteness: 93
Color: bright white (Hunter L = 90-98)		Brightness: 91-98
Electrical conductivity, μS/cm: 5		Dielectric constant: 7
MORPHOLOGY		
Particle shape: irregular	Crystal structure: gibbsite	
Particle size, μm: 0.7-55	Oil absorption, g/100 g: 12-41	Hegman grind: 5.5-6
Sieve analysis: 325 mesh residue - 0.001-0.15%		Spec. surface area, m ² /g: 0.1-12
MANUFACTURERS & BRAND NAMES:		
Alcan Chemicals, Gerrards Cross, UK Alcan AF (toothpaste grade), DH 101 (feedstock grade), FRF (general purpose), FRF LV (particle size optimized to give higher loading), ULV (optimized morphology for high loading and reduced viscosity), CV (modified particle shape improvement of cure time and lower viscosity), Precipitated (rounder particles offer denser particle packing and lower viscosity), Superfine (small particle size 0.5-1.2 μm E grades have much lower ionic impurity for electrical insulation), and Ultrafine (low Na ₂ O content for application in cables), Flamtard S (zinc stannate), H (zinc hydroxystannate), HB1 (zinc hydroxystannate/zinc borate blend), Z10 & Z15 (zinc borate). Flamtard additives enhance performance of ATH. Cera Hydrate (abrasive)		
Amspec Chemical Corporation, Gloucester City, NJ, USA Hydromax 100, 109		
Charles B. Chrystal Co., Inc., New York, NY, USA Aluminum trihydroxide		
Franklin Industrial Minerals, Nashville, TN, USA DH 35, 55, 80, 100, 200, 280, 500 (number = median particle size x 10)		
Hitox Corporation, Corpus Christi, TX, USA Haltex 302, 310, 304		
continues on the next page		

MANUFACTURERS & BRAND NAMES: Huber, J.M., Macon, GA, USA PATH 6, 9, 9HB (optimized as partial replacement of TiO ₂ in coating applications) Martinswerk, Bergheim, Germany Martinal ON-921, OL 104, OL111 Nabaltec GmbH, Schwandorf, Germany Apyral 1, 2, 3, 4, 8, 15, 16, 24, 22, 40, 60, 90, 120 (number = specific surface x 10)
MAJOR PRODUCT APPLICATIONS: carpet backing, coatings, PU-foam, pultrusion, laminates, composites, conveyor belts, cables, flooring, chipboard, tub and shower stalls, coated fabrics, electrical products, polishing, exterior cladding, tiles, synthetic marble, adhesives, coatings and sealants, sheet molding compounds, toothpaste
MAJOR POLYMER APPLICATIONS: polyester, epoxy, acrylic, PVC, PP, PE, EVA, polyurethanes, phenolics

The production process for aluminum trihydroxide might be considered a spin off of aluminum metal production where in the first phase, the metallurgical grade of aluminum trihydroxide is produced.³⁸ At the same time, this grade contains numerous impurities and requires purification. Filler grade production is a separate from the production of the metallurgical grade and yields a pure aluminum trihydroxide. Two properties made aluminum trihydroxide very popular: its flame retarding abilities and its low absorption of UV.

The low absorption of UV makes it a suitable material for applications in UV curable materials. Its flame retarding activity is due to cooling, barrier layer formation, and dilution. The cooling capability of aluminum trihydroxide comes from its ability to release water at elevated temperatures with peak release at around 300°C. The reaction by itself is endothermic and, in addition, water must be evaporated which consumes additional heat energy. Aluminum trihydroxide, after it has been decomposed, forms a barrier which slows the flow of oxygen and formation of gases. Large quantities (e.g., 150 phr) of filler must be used to obtain flame retarding properties (dilution factor). This provides flame retardancy but affects the mechanical and rheological properties of materials. Since the amounts of filler cannot be significantly reduced, additives such as compounds of zinc are used which allow for some reduction in Al(OH)₃ concentration. Mechanical properties are improved by the morphology and surface coating of the filler. Grades are available which can be used with many plastics without a fear of degrading their mechanical performance. The problem of rheology of materials during processing and use is addressed by the modification of the morphology of particles and with additives which help to reduce viscosity.

Figures 2.2 and 2.3 show how morphology might be tailored to improve viscosity. Figure 2.2 shows a precipitated grade which is composed of blocky round particles. The careful selection of an appropriate particle size distribution of these morphologically different species resulted in a low viscosity material. Figure 2.3 shows another grade which has platy particles which give a higher viscosity (as might be expected).

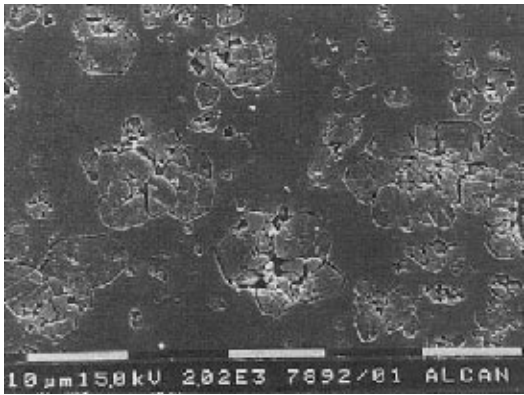


Figure 2.2. SEM of aluminum trihydroxide decreasing viscosity. *Courtesy of Alcan Chemical Europe, Gerrards Cross, UK.*

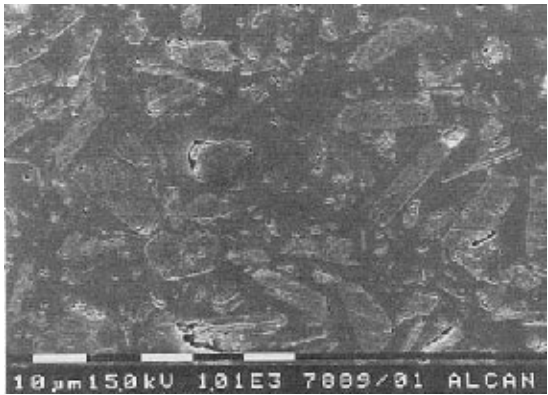


Figure 2.3. SEM of aluminum trihydroxide increasing viscosity. *Courtesy of Alcan Chemical Europe, Gerrards Cross, UK.*

2.1.5 ANTHRACITE⁴³

Names: anthracite, semi-anthracite coal, bituminous coal		CAS #: 8029-10-5
Chemical formula: C		Functionality: OH
Chemical composition: carbon - 77%, ash - 6-16%		
Trace elements: sulfur - 0.23-1.2%, silica oxide - 2.2-5.4%, alumina - 2%, ferric oxide - 0.4%		
PHYSICAL PROPERTIES		
Density, g/cm³: 1.31-1.47	Mohs hardness: 2.2	
CHEMICAL PROPERTIES		
Moisture content, %: 0.5-4	pH of water suspension: 7-7.5	Volatiles content, %: 0.5-20
ELECTRICAL PROPERTIES		
Resistivity, MΩ-cm: 50		
MORPHOLOGY		
Sieve analysis: residue on 325 mesh - traces		Particle shape: irregular
MANUFACTURERS & BRAND NAMES: Anthracite Industries, Inc., Sunbury, PA, USA 4072-C, 505, 7002, 7004, Anthrin Filler, Carbon Filler Oxide Coal Fillers, Inc., Bluefield, VA, USA Austin Black - low specific gravity reinforcing and mineral filler Keystone Filler & Manufacturing Company, Muncy, PA, USA Mineral Black 121 OC, 123, 126, 325BA		
MAJOR PRODUCT APPLICATIONS: liner, battery cases		
MAJOR POLYMER APPLICATIONS: rubber, EPDM, PP, PE		

Anthracite abounds as a mineral and can be cost-effectively mined and ground. It was found⁴³ that materials containing it have improved strength, stiffness, environmental stress cracking, heat deflection temperature, antistatic properties, weathering resistance, and chemical resistance even if filled with substantial quantities of anthracite (up to 60 wt%). The disadvantages are color, flowability of melt, and increased moisture absorption. One major advantage creates growing interest. Most fillers used today are non-combustible and remain as ash when plastic materials are incinerated at the end of several recycling operations. Anthracite has, by comparison, a very low ash content and provides calorific value.

2.1.6 ANTIMONATE OF SODIUM

Name: sodium antimonate	
Chemical formula: NaSbO ₃	Functionality: ONa
Chemical composition: Sb ₂ O ₃ - 70-73%, Sb ₂ O ₅ - 80%, NaSbO ₃ - 95%	
Trace elements: As - 0.3-0.5%, Pb - 0.6-1%, Fe - 0.004-0.0055%, Cu - 0.004%	
PHYSICAL PROPERTIES	
Density, g/cm ³ : 4.8	
CHEMICAL PROPERTIES	
Chemical resistance: it is soluble in, and reactive with, acids	
Moisture content, %: 0.5-3	Acid soluble matter, %: 100
OPTICAL PROPERTIES	
Refractive index: 1.75	Color: white to light tan
MORPHOLOGY	
Sieve analysis: 325 mesh residue - 12-45%	
MANUFACTURERS & BRAND NAMES: Laurel Industries, Cleveland, OH, USA Thermogard FR United States Antimony Corporation, Thompson Falls, MT, USA Montana Brand Sodium Antimonate Grade 1	
MAJOR PRODUCT APPLICATIONS: chemical intermediate in production of antimony pentoxide; flame retardant in plastics, paints, textiles	
MAJOR POLYMER APPLICATIONS: PBT, PET, PC, UHDPE, rubber	

Sodium antimonate must be used with halogen containing compounds for it to act as effective fire retardant. The source of chlorine may come from polymer (e.g., PVC, chlorinated rubber, etc.) or other chlorinated or brominated material. The benefits of using sodium antimonate over antimony oxide include its low tinting strength and the acid scavenging capability. For these reasons, it is used in semi-opaque or dark colored materials and in polymers such as polyesters and polycarbonates which are acid sensitive.

2.1.7 ANTIMONY PENTOXIDE

Name: antimony pentoxide		CAS #: 1314-60-9
Chemical formula: Sb ₂ O ₅ or HSb(OH) ₆ in hydrated form		Functionality: OH
Chemical composition: Sb ₂ O ₅ - 92-95%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 3.8		Melting point, °C: 380
CHEMICAL PROPERTIES		
Chemical resistance: soluble in hot acid		
Moisture content, %: 0.2-1%	pH of water suspension: 2.5-9	
OPTICAL PROPERTIES		
Refractive index: 1.7	Tinting strength: low	Color: white to yellow
MORPHOLOGY		
Particle size, µm: 10-40, 0.025-0.075 (colloidal)		
MANUFACTURER & BRAND NAMES: The PQ Corporation, Valley Forge, PA, USA Nyacol Aqueous Dispersions: A1530, A1540N, A1550 (last two digits give oxide concentration) Nyacol Organic Dispersions: AB40, AP50, APE1540 (last two digits give oxide concentration) BurnEx Powders: Plus A1588LP, Plus A1590, ZTA BurnEx Nano-Dispersible Powders: A1582, ADP480, ADP494 (for dispersions in water, non-polar solvents, and polar solvents, respectively) BurnEx 2000: 10, 20 (dispersed in PP of nano-dispersible grade and organic bromine compound)		
MAJOR PRODUCT APPLICATIONS: textiles, coatings, nonwovens, adhesives, fibers (carpet, draperies, clothing), polyester laminates, wallcoverings, wire insulation, office furniture, automotive interiors, electrical housings, computers, printers, appliances, telecommunication, film, sheet		
MAJOR POLYMER APPLICATIONS: epoxy, polyester, PVC, ABS, HIPS, PP		

Antimony pentoxide is an alternative to antimony trioxide. It finds applications in semi-transparent materials and dark colors because of its low tinting strength. As with antimony trioxide, antimony pentoxide must be used together with halogen-containing compounds to function as a flame retardant (see discussion under antimony trioxide). The other advantages of antimony pentoxide include its refractive index which is closer to most materials, its very small particle size, its high specific surface area, and its substantially lower density. Because of its small particle size, it is frequently used in the textile industry since its addition has only a small effect on color or on mechanical properties. Production of fine-denier fibers requires a stable dispersion and a small particle size filler. The flame retardancy of laminates is also improved with antimony pentoxide because small particles are easier to incorporate in the interfiber spaces.

Antimony pentoxide, as an additive for plastic materials such as polyolefins and ABS, is produced in predispersed form containing halogen compounds and a polymeric binder which has a low melting index to aid incorporation.

Incorporation of aqueous dispersions of antimony pentoxide into latex requires a pH adjustment prior to adding it to latex to prevent latex coagulation. Dispersions of antimony pentoxide usually have a $\text{pH} = 5$ which is too low for use in most latex formulations. Adjustment of pH can be made with ammonia but prior to such a pH adjustment it is necessary to dilute the dispersion to a concentration below 40% Sb_2O_5 .

The use of particulate Sb_2O_5 in plastics extrusion requires that some precautions be taken. The extruder temperature setting must be below the level which degrades halogen-containing additive ($180\text{-}250^\circ\text{C}$). The vented extruder should be used to remove free moisture. The antimony pentoxide must be kept sealed when not in use to prevent moisture pickup and dust generation should be prevented during handling. If antimony pentoxide is used in materials which do not contain halogen, the formulation should include sufficient halogen-containing additive to provide halogen/antimony mole ratio of 3/1.

2.1.8 ANTIMONY TRIOXIDE³⁹⁻⁴²

Name: antimony trioxide		CAS #: 1309-64-4
Chemical formula: Sb ₂ O ₃		Functionality: none
Chemical composition: Sb ₂ O ₃ - 98-99.5%		
Trace elements: As - 0.02-0.2%, Pb - 0.04-0.3%, Fe - 0.004-0.01%, Se - 0.005%, SO ₄ - 0.002-0.05%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 5.2-5.67		Melting point, °C: 656
CHEMICAL PROPERTIES		
Chemical resistance: reactive with acids and bases		
Moisture content, %: 0.1	Water solubility, %: 0.001	
pH of water suspension: 2.0-6.5	Acid soluble matter, %: 100	
OPTICAL PROPERTIES		
Refractive index: 2.087		
Color: white		Tinting strength: high to low
MORPHOLOGY		
Crystal structure: cubic or orthorhombic		Specific surface area, m ² /g: 2-13
Sieve analysis: 325 mesh residue - 0.1-0.5%		Particle size, µm: 0.2-3
MANUFACTURERS & BRAND NAMES: AMSPEC Chemical Corporation, Gloucester City, NJ, USA KR (excellent whiteness and tinting strength), KR - Superfine (small particle size for fiber and film), LTS (low tint for darker colors), AMSTAR (utility grade for cost effective applications) Laurel Industries, Cleveland, OH, USA FireShield H (high tint strength), L (low tint strength), HMP (high purity, low trace metals), UltraFine (low particle size, 0.2-0.4 µm gives reduced loss of mechanical properties, and higher tinting strength than H) United States Antimony Corporation, Thompson Falls, MT, USA VF (very fine), MP (micro pure), HT (high tint), LT (low tint), Industrial Grade		
MAJOR PRODUCT APPLICATIONS: plastics, textiles, paper, paints, rubber, UV resistant pigments		
MAJOR POLYMER APPLICATIONS: PA, PVC, PP, PE, ABS, HIPS, polyester, polyurethanes, rubber, epoxy		

Antimony oxide is usually produced from stibnite (antimony sulfide) or by oxidizing antimony metal.

Many theories attempt to explain the mechanism of flame retardancy. The flame retarding action is thought to take place in the vapor phase above the burning surface. For antimony oxide to work, the halogen and antimony oxide must be found in a vapor phase which will occur at temperatures above 315°C. At these temperatures, antimony halides and oxyhalides are formed and act as flame extinguishing moieties by quenching radicals as they form.

The tinting strength depends on particle size. If particle sizes are below 300 nm they fall below visible range. Above this value, tint strength decreases as the particle size increases. The high tint strength grade usually has particle sizes in a range of 1.1-1.8 μm and the low tint strength grade has particle sizes in a range of 1.8-3 μm . The tint strength can also be affected by crystalline form. The orthorhombic form decreases tint strength.

Different formulations are needed for individual polymers (according to the manufacturer AMSPEC). These concentrations are recommended: PVC: Sb_2O_3 - 2-10 phr; PP: Sb_2O_3 - 2-4 phr, brominated organic 4-22 phr; ABS: 4:1 organo-Br/ Sb_2O_3 ; HIPS: Sb_2O_3 - 4 phr, aromatic bromine - 12 phr, polyurethanes: 5-15 phr Sb_2O_3 and 5-15 phr halogenated compounds.

The manufacturers offer a wetted grade of antimony oxide to reduce dust. This is made by the addition of 3-4% plasticizer (DIDP, DOP, DINP, or ethylene glycol). Concentrates are produced by manufacturers and specialized companies. United States Antimony Corporation manufacturers concentrates with up to 90% active component. Laurel Industries produce both antimony oxide and organic flame retardants which are sold separately and in ready to use combinations which also include resin carriers. Paraffin is a convenient binder for extrusion and molding applications. Arethon International Plastics Ltd. has a full range of flame retardant masterbatches which are marketed under the brandname Areflam. The active content in these masterbatches is from 50 to 80%. They are prepared with more than 10 carrier resins and have the correct content of halogen-containing material and Sb_2O_3 or, in the case of halogen-free masterbatch, appropriate amount of $\text{Al}(\text{OH})_3$.

Antimony oxide can be advantageously combined with huntite/hydro-magnesite fillers to offer excellent flame retarding properties.^{39,42} Also, zinc borate can be used to reduce the amount of antimony trioxide. Other performance enhancing additives include zinc stannate and ammonium octamolybdate.⁴⁰

2.1.9 APATITE⁴⁴⁻⁴⁵

Names: apatite, calcium (fluoro, chloro, hydroxyl) phosphate		
Chemical formula: Ca ₅ (PO ₄) ₃ (OH,F,Cl)		Functionality: OH, CL, F
PHYSICAL PROPERTIES		
Density, g/cm ³ : 3.1 - 3.2	Mohs hardness: 5	
OPTICAL PROPERTIES		
Color: white to yellow		Brightness: 58-63
MORPHOLOGY		
Particle size, μm: 43	Crystal structure: hexagonal	Cleavage: basal direction
MAJOR PRODUCT APPLICATIONS: paper, medical (replacement bones)		
MAJOR POLYMER APPLICATIONS: PMMA		

2.1.10 ASH, FLY⁴⁶⁻⁴⁹

Names: fly ash		CAS #: 60676-86-0
Chemical formula: variable composition		Functionality: variable
Chemical composition: SiO ₂ -30-60%, Al ₂ O ₃ - 11-19%, Fe ₂ O ₃ - 4-11%, MgO - 5-6%, CaO - 2-45%		
Trace elements: sodium, boron, potassium, strontium, barium, molybdenum, lithium, vanadium, chromium		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.1-2.2		
CHEMICAL PROPERTIES		
Moisture content, %: 2-20		
MORPHOLOGY		
Particle shape: irregular	Particle size, µm: 4	Porosity: high
Sieve analysis: residue on 325 mesh sieve - 5%		
MAJOR PRODUCT APPLICATIONS: concrete modification, composite, building materials, polyester mortar		
MAJOR POLYMER APPLICATIONS: PP, PE, PU, PET		

Fly ash may become more extensively used as a inexpensive filler. It is not used in large quantities at the present time. Research studies⁴⁶⁻⁴⁹ show that materials can be improved when fly ash is used as a filler. The major hurdle is health and safety since fly ash contains crystalline silica and is, consequently, considered a hazardous material.

2.1.11 ATTAPULGITE

Names: attapulgite, hydrous magnesium aluminum silicate, Fuller's earth, palygorskite, clay		CAS #: 12174-11-7
Chemical formula: variable composition		Functionality: OH
Chemical composition: SiO ₂ - 50-68%, Al ₂ O ₃ - 9-12%, MgO - 3-12%, Fe ₂ O ₃ - 3-5%		
Trace elements: potassium, sodium, magnesium		
PHYSICAL PROPERTIES		
Density, g/cm³: 2.3-2.4	Mohs hardness: 1-2	Loss on ignition, %: 5-23
CHEMICAL PROPERTIES		
Moisture content, %: 2-16	Adsorbed moisture, %: 1-6	pH of water suspension: 6.5-9.5
Volatiles content, %: 5-15		
OPTICAL PROPERTIES		
Color: buff, tan, cream		Refractive index: 1.57
MORPHOLOGY		
Particle shape: irregular, needle	Crystal structure: monoclinic	Oil absorption, g/100 g: 60-120
Particle size, μm: 0.1-20	Specific surface area, m²/g: 120-400	
Sieve analysis: residue on 325 mesh sieve - 0.01-8		
MANUFACTURERS & BRAND NAMES: Milwhite, Inc., Houston TX, USA Attapulgite A, LMV, RVM, Basco Salt Mud, Econosorb, Fertogel, Gel B, Gel 420-P, Gel 540-P, Gel 601-P, High Yield Attapulgite, Milfines, Milsorb, Milsorb-CG, Supper Gel B Non-Metals, Inc., Affiliate of The China Non-Metallic Minerals, Tucson, AZ, USA Attapulgite clay for paint, adsorbent, drilling mud, and fertilizer		
MAJOR PRODUCT APPLICATIONS: pesticides, herbicides, fertilizers, absorbents, drilling mud, joint compounds, neutralizers, asphalt thickeners, adhesives, paints, coatings, sealants, environmental remediation materials, antidiarrheal medication, gels		

Attapulgite is naturally occurring crystalline hydrated magnesium aluminum silicate. It has a unique three-dimensional chain structure giving unusual colloidal and sorptive properties. Attapulgite is in the range of clay minerals classified as Fuller's earth. The natural mineral is ground, classified, and thermally activated. A high temperature drying produces LVM grade (LVM standing for low volatile matter) and having up to 1% of free moisture and up to 5% of total volatiles. Low temperature drying produces thickeners having up to 12% of free moisture and sorptive products of regular volatile matter, RVM, having 6% free moisture and up to 9% volatiles. Granular grades are manufactured by two basic methods: one includes drying or calcination, followed by grinding and screening to the size; in the other, a raw clay is pugged, extruded, dried or calcinated, followed by grinding and screening. Grades produced by the first method are designed as “A”, whereas

extruded grades are “AA”. Thus there are four different grades available: AA RVM, A RVM, AA LVM, and A LVM differing in water disintegrability. LVM grades resist disintegration in water whereas RVM grades do not.

There is a wide range of average particle sizes (0.1-20 μm) available. However, most commonly used products are in the range of 0.1-3 μm . Small particle size and high porosity result in a very high BET surface area (120-150 m^2/g) and an unusually high oil absorption in a range from 60 to 120%. Attapulgites are unusual in these respects. Also pH, which is in the range of 7.5-9.5, differs from that of kaolins.

Figure 2.4 shows the morphology of attapulgite which reveals the reasons for its high absorptivity.

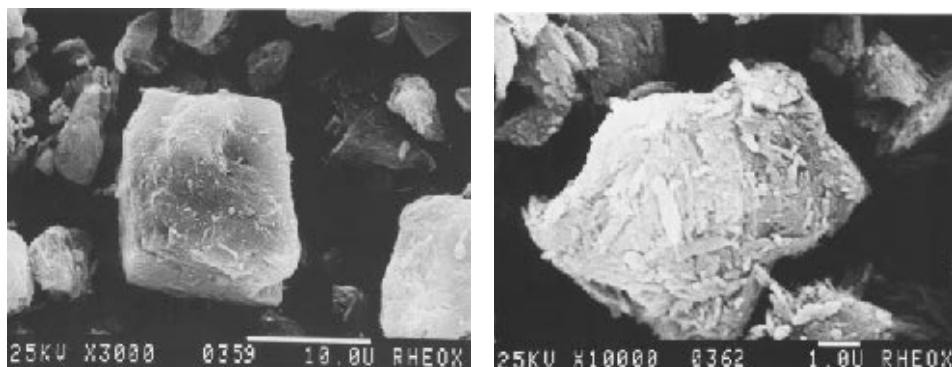


Figure 2.4. SEM micrograph of Attagel 50. *Courtesy of Rheox, Inc., Hightstown, NJ, USA.*

2.1.12 BARIUM METABORATE

Name: barium metaborate monohydrate		CAS #: 13701-59-2
Chemical formula: BaB ₂ O ₄ ·H ₂ O		Functionality: OH
PHYSICAL PROPERTIES		
Density, g/cm ³ : 3.3	Fusion point, °C: 900-1050	
CHEMICAL PROPERTIES		
pH of water suspension: 9.8-10.3		
OPTICAL PROPERTIES		
Refractive index: 1.55-1.60		
Color: white		
MORPHOLOGY		
Oil absorption, g/100 g: 30		
MANUFACTURER & BRAND NAME: Buckman Laboratories, Memphis, TN, USA Busan 11-M1		
MAJOR PRODUCT APPLICATIONS: paints, coatings, sealants		
MAJOR POLYMER APPLICATIONS: alkyd resin, polyurethane, acrylic		

Barium metaborate is a truly multifunctional additive which inhibits corrosion, increases UV stability, inhibits mold growth, and has flame retarding properties when used in combination with halogenated materials. The commercial product of Buckman Laboratories is a modified product which contains 90% of active ingredient.

2.1.13 BARIUM SULFATE⁵⁰⁻⁵⁷

Names: barium sulfate, barite, blanc fixe		CAS #: 7727-43-7
Chemical formula: BaSO ₄		Functionality: none if not surface grafted
Chemical composition: BaSO ₄ - 86-99%, SrSO ₄ - 1-2%, CaO - 0-10.8%, Fe ₂ O ₃ - 0.1-1.4%, SiO ₂ - 0.9-2.1%		
Trace elements: iron, copper, manganese, and lead		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 4.0-4.9	Mohs hardness: 3-3.5	Melting point, °C: 1580
Linear coefficient of thermal expansion, 10 ⁻⁶ 1/K: 10		Loss on ignition, %: 0.2-2.6
CHEMICAL PROPERTIES		
Chemical resistance: resistant to acids and alkalis		
Moisture content, %: 0.1-0.3	Acid soluble matter, %: traces	Volatiles content, %: 0.1-0.5
Soluble content, %: 0.00025-0.4	Water solubility, ppm: 3	pH of water suspension: 6-9.5
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 1.64		Whiteness: 94-96
Color: white		Brightness: 65-99
Tinting strength: medium		Reflectance: 90
Dielectric constant: 11.4	Resistivity, Ω: 19.075	Conductivity, μS/cm: 200-300
MORPHOLOGY		
Particle shape: depends on grade	Crystal structure: orthorhombic	Oil absorption, g/100 g: 8-28
Particle size, μm: 3-30 (barites and some synthetic grades), 0.7 (blanc fixe), <0.1 (special grades)		
Sieve analysis: residues on 325 mesh sieve - 0.01-12%, 0.001% (blanc fixe)		Cleavage: one direction
Specific surface area, m ² /g: 0.4-31		Hegman fineness: 2.5-7
MANUFACTURERS & BRAND NAMES: Barium and Chemicals, Inc. Steubenville, OH, USA Barium Sulfate, 98% Technical Precipitated Grade CIMBAR, Cartersville, GA, USA Bara 2002C, 325C, 200N, 325N, 200M, 325M (industrial grade ground barites) Bariace B-30, B-34 (surface treated barium sulfate with SiO ₂ -Al ₂ O ₃ to improve abrasiveness, dispersion, gloss, and hardness; particle size 0.3 μm) Barifine, BF-1, BF-10, BF-20, BF21 (ultrafine barium sulfates in particle range of 0.03-0.06 μm, improve dispersion of pigments and prevent flocculation) Barimite UF, XF, 22, 200, G-50 (flotation grade barites) CIMBAR 325, XF, CF, UF, EX (high purity white barites) Polywate (low BaSO ₄ content materials, filled foam market)		

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MANUFACTURERS & BRAND NAMES:
Hitox Corporation, Corpus Christi, TX, USA Bartex 10, 65, 80, OWX - barium sulfate for a broad range of applications, including TiO ₂ replacement
J.M. Huber Corporation, Macon, GA, USA Huberbrite 1, 3, 7, 10, 12 (milled barite, the number refers to median particle size)
Milwhite, Inc., Houston, TX, USA Basco Wate (ground barite for drilling fluids) Blanca 2, 4, 8 (high quality ground barites; number refers to particle size) Marfil 2, 4, 8, 10, 20, 40 (natural ground barite for coatings and plastics, number refers to particle size)
Nippon Chemical Industry Co., Japan Barium sulfate AD
Polar Minerals, Mt. Vernon, IN, USA 1000 Series includes barites 1075, 1065, 1040 of different particle sizes for paints and coatings 2000 Series includes barites 2075, 2065, 2010 of different particle size for plastics, paints, and brake linings Blanc Fixe 1090P - precipitated barium sulfate
Sachtleben Chemie GmbH, Duisburg, Germany Albaryt and Albaryt Plus (wet processed and chemically bleached grades) Barytmehl F, N, G, 901 (natural ground white barites with different particle sizes, F - fine, N - medium, G - coarse) Blanc fixe N, F, micro (standard grades) Blanc fixe, HXH, HNF (finely precipitated barium sulfate of extremely high purity and brightness) Drilling mud grade BS EWO (wet processed and chemically bleached grade, slightly coarser than Albaryt) Fleur (wet processed and chemically bleached grade slightly coarser than Albaryt and EWO) Ground Barites C 101, CH 1177, C 7, C 14, TS (fine powders made by grinding with a lower brightness than Barytmehl but comparable particle sizes) K1, K2, K3, K4, M (high purity, synthetic grades having a high brightness (96-98) and high refractive index) Sachtoperse HP, HU-N, HU-D (smallest particle size grades from below 0.1 to 0.2 µm, used as nucleating agents and anti-flocculating additives)
ZEMEX Industrial Minerals, Atlanta, GA, USA Cherokee 289, 290, 291 (ground barites)
MAJOR PRODUCT APPLICATIONS: paints, inks, wood finishes, powder coatings, adhesive, mastics, seals, sealants, coatings, medical, paper, battery products, drilling fluids, brake linings, bowling balls, sound dampening, plastisols, urethane foams, acoustical compounds, insulating materials
MAJOR POLYMER APPLICATIONS: PET, PVC, melamine, polyurethanes, alkyd

Barites are the most common barium minerals, found in pure form but also together with many other minerals. The most frequent replacement for barium is that of strontium or radium. Barium sulfate, widely used in industry and in medical applications, originates from natural barites and synthetic materials. The quality of the filler depends on the purity of material used for production and the method of processing (a chemical purification is a complex process which determines the quality of synthetic or reprocessed material). The simplest method of processing includes grinding and dry classification. Finer products are obtained by concentration, wet grinding, bleaching, and classification. The product of highest quality is *blanc fixe* (permanent white). It is produced from the reaction between barium carbonate and sulfuric acid. Since the only other reaction products are water

and carbon dioxide, product purity depends on the quality of raw materials used. The particle size distribution depends on process parameters, including the concentration of reactants, the rate of addition, temperature, and efficiency of mixing. These parameters are easily regulated, so particle size distribution. In some applications, the filler must have a narrow range of particle size distribution. The average particle size diameter for natural products is usually in a range from 2 to 30 μm (maximum particle size: 15-75 μm). The price is related to the average particle diameter. *Blanc fixe* being the smallest is most expensive (the average diameter of particles ranges from 0.1 to 4 μm). Oil number depends on particle size, and for *blanc fixe* it is in a range from 12 to 28 g/100 g, whereas for natural products, it is lower, in a range from 7 to 12 g/100 g. Particles are non-porous and of irregular shape in the case of natural product, whereas *blanc fixe* is almost spherical.

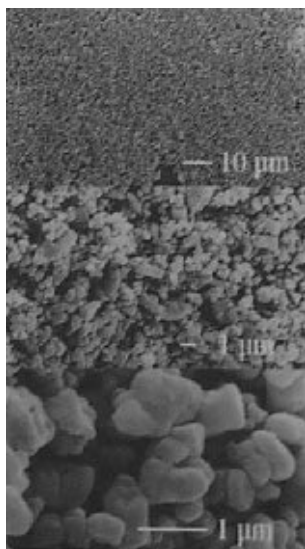


Figure 2.5. SEM micrograph of Blanc fixe micro at different magnifications (upper 1000x, middle 5000x, lower 25,000x). Courtesy of Sachtleben Chemie, Duisburg, Germany.

Further information on morphology is discussed below based on electron microscopy data. Figure 2.5. shows morphology of blanc fixe. The particle size of blanc fixe (0.7 μm) is comparable with the particle size of titanium dioxide (0.3 μm). Comparison of blanc fixe with another synthetic grade of barium sulfate, barium sulfate K2, produced by Sachtleben Chemie shows a difference in particle size but the morphological structure is quite similar (Figure 2.6). Figure 2.7 shows a still finer grade developed by Sachtleben Chemie which has particle size similar to titanium dioxide (0.35 μm). This is a quite extraordinary filler which has core made out synthetic barium sulfate (an insulator) coated with a semi-conducting layer of antimony doped with SnO_2 (Sacon P401). This material has high brightness, electric conductivity, and light transparency in thin coatings. The material is used to eliminate static charges from plastics and painted surfaces. At approximately 19% PVC material has a percolation threshold and surface resistivity drop rapidly by 8 orders of magnitude. Sachtoperse is still smaller in particle size, from 0.2 μm to below 0.1 μm , depending on grade. This is used as nucleating

additive to polymers, such as PET. It decreases cycle time and reduces processing temperature, increases crystallization rate, and prevents flocculation of pigments. Figure 2.8 explains the mechanism by which Sachtoperse prevents pigment flocculation. Pigment particles (lighter particles) adhere to Sachtoperse (smaller darker particles) which act as a spacer. This process results in brighter colors and improved gloss.

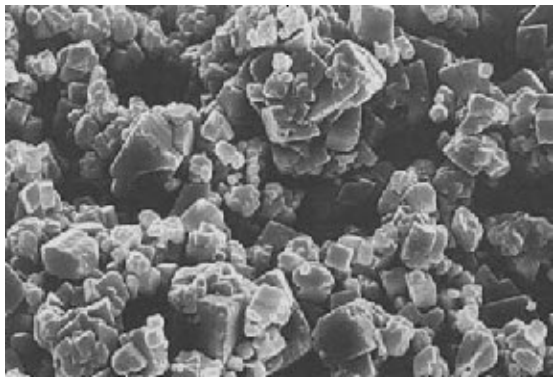


Figure 2.6. SEM micrograph of K2 grade at 2000x magnification. *Courtesy of Sachtleben Chemie, Duisburg, Germany.*

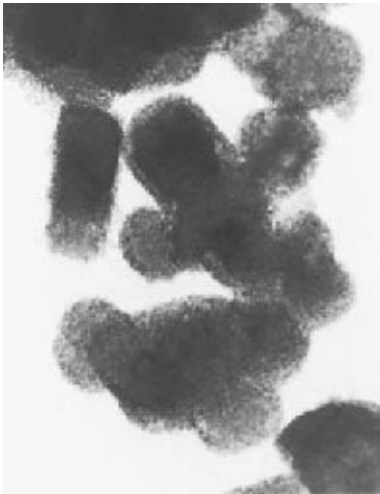


Figure 2.7. TEM micrograph of Sacon P 401 at magnification of 350,000. *Courtesy of Sachtleben Chemie, Duisburg, Germany.*



Figure 2.8. Anti-flocculating action of Sachtoperse HU. *Courtesy of Sachtleben Chemie, Duisburg, Germany.*

When images of synthetic grades are compared with image of ground barites (Figure 2.9), the morphological differences become apparent. These differences are not simply in particle size and distribution but also in the shape of particles.

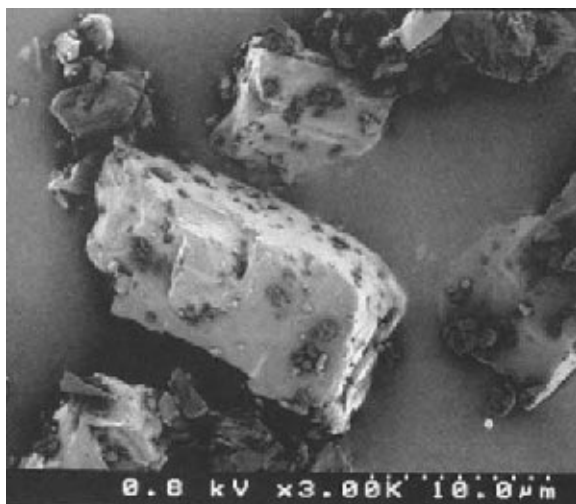


Figure 2.9: SEM micrograph of milled barite, Huberbrite. *Courtesy of J. M. Huber Corporation, Macon, GA, USA.*

Chemical composition is another factor which determines quality, particularly in chemical and medical applications but also in paints and coatings where it affects brightness. Barium is highly toxic but only in the form of water soluble salt; therefore in every application the water soluble barium must be controlled. Other usual admixtures contain iron, copper, manganese, and lead, and depending on application, their concentration is also restricted. Natural products contain 94-99% BaSO_4 , whereas *blanc fixe* contains from 97.5 to over 99%.

For some applications, a refractive index is important. A match between the particle size of some barium grades and the refractive index of matrix material allows the formulation of products with desirable optical properties. A series of synthetic barium sulfates is produced by Sachtleben Chemie which have particle sizes between 4 and 10 μm . If the particle size of these barium sulfates is well coordinated with the refractive index of the matrix polymer, semi-opacity combined with translucency results. This permits the formulation of a light disperser in lampshades or in illuminated advertising displays. The correct particle size can be calculated from the equation: $d = (100n - 141)/2$, where n is the refractive index of the resin and d the particle size of barium sulfate.

Barium sulfate has found many applications mainly because of its unique chemical resistance and inertness (for example, it is not affected by acid rain). The other reason for its frequent application is high absorptivity of light and, significantly, X-rays (for use in X-ray detectable materials).

2.1.14 BARIUM & STRONTIUM SULFATES

Name: barium strontium sulfate natural blend		
Chemical formula: BaSO ₄ & SrSO ₄		Functionality: none
Chemical composition: SrSO ₄ /BaSO ₄ - 87-95%, CaCO ₃ - 2.6-5%, CaO - 1.9-2.5%, Fe ₂ O ₃ - 0.1-1.7%, CaSO ₄ - 0.7-3%, SiO ₂ - 0.1-1%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 3.8-3.9		
CHEMICAL PROPERTIES		
Chemical resistance: similar to BaSO ₄		
Moisture content, %: <0.3	pH of water suspension: 7-7.5	
OPTICAL PROPERTIES		
Color: white		Reflectance, %: 86-88
MORPHOLOGY		
Particle size, μm: 11-20	Crystal structure: rhombic	Oil absorption, g/100 g: 9.5-11.5
Sieve analysis: retained on 325 mesh sieve - 0.1-2%		Hegman fineness: 3.5
MANUFACTURER & BRAND NAME: Milwhite, Inc., Houston, TX, USA Microwate 10, 20, 40 (natural ground product)		
MAJOR PRODUCT APPLICATIONS: plastics, paints, cellular foams		

2.1.15 BARIUM TITANATE⁵⁸

Names: barium titanate	
Chemical formula: BaTiO ₃	Functionality: none
Chemical composition: BaTiO ₃ - 98.9-99.5%	
Trace elements: Sr, Ca, Nb, Fe, Si, Al, Mg, Na	
PHYSICAL PROPERTIES	
Fusion point, °C: 1250	Loss on ignition, %: 0.8
CHEMICAL PROPERTIES	
Moisture content, %: 0.2	
OPTICAL & ELECTRICAL PROPERTIES	
Refractive index: 2.4	Dielectric constant: 3.8
MORPHOLOGY	
Particle size, µm: 0.07-2.7	Specific surface area, m ² /g: 2.4-8.5
MANUFACTURERS & BRAND NAMES: Cabot Performance Materials, Boyertown, PA, USA Hydrothermal Barium Titanate (barium titanate of small particle size obtained by a hydrothermal method) TAM Ceramics, Niagara Falls, NY, USA Ticon HPB, HPB-B, TME, F (high purity grades) Ticon C, P, T (solid state grades) Ticon 5016 (solid state, high purity grade) Ticon COF-40, COF-50, COF-70, CN (solid state niobium-doped grades)	
MAJOR PRODUCT APPLICATIONS: thermistors, capacitors, optics, ferroelectric ceramics, filler for ferroelectric polymers, pyro and piezoelectric composites	
MAJOR POLYMER APPLICATIONS: poly(vinylidene fluoride)	

2.1.16 BENTONITE⁵⁹⁻⁶⁶

Names: bentonite, clay, montmorillonite, Na-montmorillonite, Ca-montmorillonite, hydrated sodium calcium aluminum magnesium silicate hydroxide		CAS #: 1302-78-9
Chemical formula: (Na, Ca)(Al, Mg) ₆ (Si ₄ O ₁₀) ₃ (OH) ₆ ·nH ₂ O		Functionality: OH, ONa, OCa
Chemical composition: SiO ₂ - 56-72%, Al ₂ O ₃ - 13-21%, Fe ₂ O ₃ - 0.9-5%, MgO - 1.7-2.4%, CaO - 0.7-2.2%, Na ₂ O - 0.3-2.7%, K ₂ O - 0.2-0.3%		
Trace elements: AS, Ba, Cd, Pb, Se, Hg		
PHYSICAL PROPERTIES		
Density, g/cm³: 1.6 - 3	Mohs hardness: 1-2	Loss on ignition, %: 8.4-11.9
CHEMICAL PROPERTIES		
Moisture content, %: 2-14	pH of water suspension: 7-10.6	Water solubility, %: 3
OPTICAL PROPERTIES		
Color: light cream, buff to tan, light gray, white to off-white		
MORPHOLOGY		
Particle size, μm: 0.18-1	Oil absorption, g/100 g: 36-52	
Sieve analysis: residue on 325 mesh sieve - 2%		
Specific surface area, m²/g: 0.8-1.8		Hegman fineness: 2-7
MANUFACTURERS & BRAND NAMES: Charles B. Co., Inc., New York, NY, USA Wyoming Granular Bentonite, Bentonite 200, 325 (sodium bentonite) Bentonite 34, (silicate of aluminum which swells eight times the volume) Cream Bentonite (light color bentonite) Bentonite Semi-dried Crude (sodium bentonite) CIMBAR Performance Minerals, Cartersville, GA USA Organotrol 2200, 3300, 3440, 3550, 3660, SA (general purpose thickener and suspension additive) Suspengel 16, 30, 200, 325 (high purity bentonite thixotropes) Suspengel Ultra, Elite, Micro (high purity bentonite accepted for use in food) Milwhite, Inc., Houston, TX, USA Basco Gel (blended bentonite for viscosity modification) Bentonite B (calcium montmorillonite for ceramics and molding) Milbond 3 (water treatment and sealant grade) Rev-Dust (calcium montmorillonite) Non-Metals, Inc., Affiliate of The China Non-Metallic Minerals, Tucson, AZ, USA HB-Ca, JJ-Ca, JJ-Na, JL-Na, ZL-Na, LL-Ca - Ca and Na bentonites in powder form		
MAJOR PRODUCT APPLICATIONS: paints, coatings, paper, adhesives, sealants, inks, cosmetics, plastics compounding, , pharmaceuticals, foods, drilling muds, waterproofing		
MAJOR POLYMER APPLICATIONS: alkyd, polyurethane, butyl resin, PP, PS		

Bentonite is a clay derived from the weathering of volcanic ash and composed of the mineral montmorillonite. There are two varieties: sodium bentonite which has high swelling capacity in water and calcium bentonite with negligible swelling capacity. Figures 2.10 and 2.11 show the morphology of ground ore and the

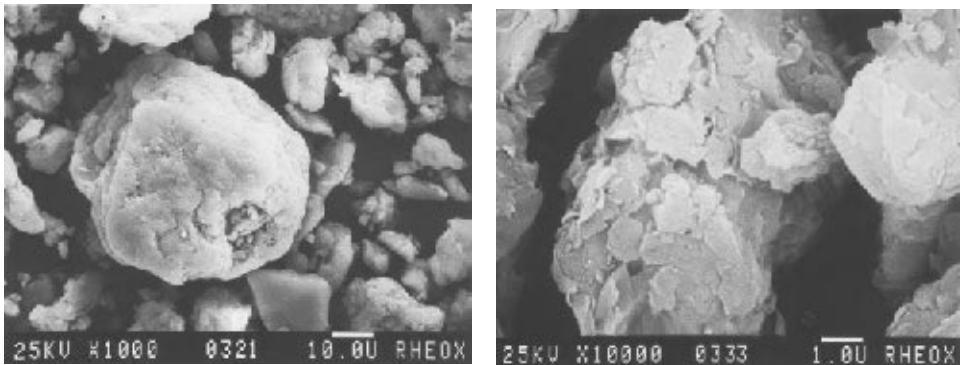


Figure 2.10. Bentonite ground ore. *Courtesy of Rheox, Inc., Hightstown, NJ, USA.*

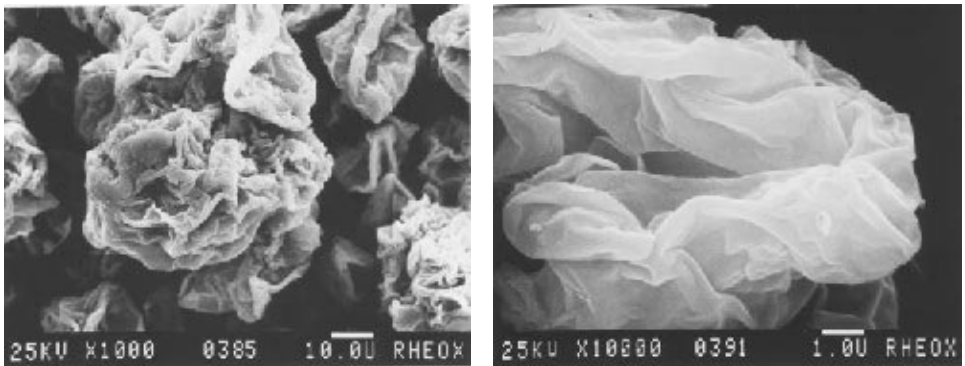


Figure 2.11. Bentonite purified and spray dried. *Courtesy of Rheox, Inc., Hightstown, NJ, USA.*

purified material. The high surface area and a structure which allows water to penetrate mineral layers are responsible for the swelling capabilities of bentonite clays.

In addition to the traditional use in paints as viscosity regulator, bentonite is currently used in the development of new materials with nanocomposite structures.

2.1.17 BERYLLIUM OXIDE

Names: beryllium oxide		CAS #: 1304-56-9
Chemical formula: BeO	Functionality: none	
Chemical composition: beryllium oxide - 99.5%		
Trace elements: Al, Ca, Mg, Si		
PHYSICAL PROPERTIES		
Density, g/cm³: 2.85	Melting point, °C: 2570	
Thermal conductivity, W/m·K: 250	Specific heat, kJ/kg · K: 1.03	
Thermal expansion coefficient, 10 ⁻⁶ 1/K: 9	Maximum temperature of use, °C: 1800	
Tensile modulus, MPa: 138	Poisson ratio: 0.26	Compress. strength, MPa: 1550
OPTICAL & ELECTRICAL PROPERTIES		
Color: white	Resistivity, Ω-cm: 10 ¹⁷	
Dielectric constant: 6.8	Dielectric strength, V/cm: 100	Loss tangent: 0.0004
MORPHOLOGY		
Particle size, µm: 20	Crystal structure: hexagonal	
MANUFACTURERS & BRAND NAMES: Accuratus Ceramic Corporation, Washington, NJ, USA San Jose Delta Associates, Inc., Santa Clara, CA, USA		
MAJOR PRODUCT APPLICATIONS: combination of extremely high thermal conductivity and excellent dielectric properties		

2.1.18 BORON NITRIDE

Names: boron nitride		CAS #: 10043-11-5
Chemical formula: BN	Functionality: none	
Chemical composition: BN - 95-99.5%		
Trace elements: Cu, Al, Mg, Fe, K, Si		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.25	Knoop hardness, kg/mm ² : 11	Specific heat, kJ/kg · K: 794
Coefficient of expansion, 10 ⁻⁶ 1/K: <1		
Thermal conductivity, W/K · m: 250-300	Maximum temperature of use, °C: 985	
OPTICAL & ELECTRICAL PROPERTIES		
Dielectric constant: 3.9	Volume resistivity, Ω-cm: 10 ¹⁵	Loss tangent: <0.0002
MORPHOLOGY		
Particle size, μm: 3-200	Crystal structure: hexagonal	Spec. surface area, m ² /g: 0.5-25
MANUFACTURERS & BRAND NAMES: Accuratus Ceramic Corporation, Washington, NJ, USA Advanced Ceramics Corporation, Lakewood, OH, USA PolarTherm 100 Series (five grades of hexagonal powders of different particle sizes) PolarTherm 300 Series (low density agglomerates) PolarTherm 600 Series (four grades of high density agglomerates) Carborundum Corporation, Amherst, NY, USA CarboTherm (seven grades of different particle sizes for refractory applications) Combat (thirteen grades of different particle sizes for liquid coatings and aerosol sprays) San Jose Delta Associates, Inc., Santa Clara, CA, USA - hot pressed boron nitride shapes		
MAJOR PRODUCT APPLICATIONS: rubber pads, liquid encapsulants, underfills, printed circuit boards, adhesives, greases, liquid coatings, aerosol sprays		
MAJOR POLYMER APPLICATIONS: silicone, epoxy		

Boron nitride filler address the “burning need” of modern electronic industry which is to protect electronic equipment from ever increasing generation of heat by high performance electronic devices. The combination of high electric resistivity with high thermal conductivity gives required performance to electronic adhesives and components.

Figure 2.12 shows SEM micrograph of boron nitride with 8-14 μm particle size.

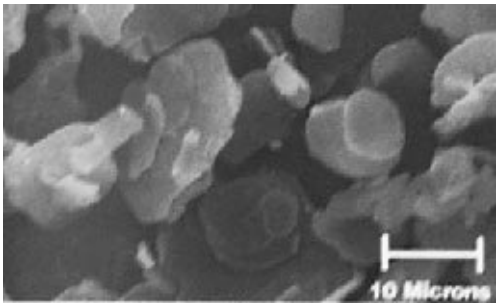


Figure 2.12. PolarTherm PT 120 boron nitride. *Courtesy of Advanced Ceramics Corporation, Lakewood, OH, USA.*

2.1.19 CALCIUM CARBONATE⁶⁷⁻¹³⁸

Names: calcium carbonate, limestone, chalk		CAS #: 1317-65-3
Chemical formula: CaCO ₃	Functionality: only from admixtures or surface treatment	
Chemical composition: CaCO ₃ - 85-99%, SrO - 0.5%, MgCO ₃ - 0.4-13%, BaO, MnO, SiO ₂ , Fe ₂ O ₃ , Al ₂ O ₃		
Trace elements: As, Ba, Hg, Pb		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.7-2.9	Mohs hardness: 3-4	Melting point, °C: 1339
Decomposition temp., °C: 1150	Loss on ignition, %: 43.5	Surface tension, mJ/m ² : 207
Thermal conductivity, W/K · m: 2.4-3	Linear coefficient of expansion, 1/K: 4.3-10 x 10 ⁻⁶	
Young modulus, MPa: 35,000	Poisson coefficient: 0.27	
CHEMICAL PROPERTIES		
Chemical resistance: reacts with acids		
Moisture content, %: 0.01-0.5	Water solubility, %: 0.99 x 10 ⁻⁸	pH of water suspension: 9-9.5
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 1.48, 1.65, 1.7	Birefringence indices: 1.48 & 1.65 (calcite)	Whiteness: 80-98
Color: white to gray	Reflectance, %: 86-94	Brightness: 82-94
Dielectric constant: 6.1	Volume resistivity, Ω-cm: 10 ¹⁰	
MORPHOLOGY		
Particle shape: irregular	Crystal structure: see text	Hegman fineness: 2-6.5
Particle size, μm: 0.2-30, 0.02-0.4 (precipitated)		Oil absorption, g/100 g: 13-21
Sieve analysis: residue on 325 mesh sieve - 0.005-14%		Specific surface area, m ² /g: 5-24
MANUFACTURERS & BRAND NAMES:		
Charles B. Co., Inc., New York, USA		
Calofort U, U70 - small particle size, high specific surface area, precipitated calcium carbonate		
Granulated Oyster Shell - low heavy metals designed for pharmaceutical applications		
Food Grade Calcium Carbonate, FCC Grade - food grades		
Ultrafine Calcium Carbonate - general purpose ground limestone		
Hiflex - surface treated calcium carbonate for easy compounding in water pipes, cables, etc.		
Precipitated USP Grade - 3 grades for pharmaceutical, cosmetic, and food industries		
402 - surface modified calcium carbonate for PVC plastisols and other plastics		
ECC International, Cornwall, UK		
Carbital 110S, 110, 120 - high whiteness grades for PP derived from Italian marble (S stearate coating)		
Polcarb 60 & 90 - PVC extrusion, plastisol and PP sheeting		
Queensfil 25, 240, 300 - footwear, latex, PE masterbatch, PA moldings, all PVC applications		
Polcarb S, SB, 40S, 60S (stearate coated) - cable, extrusion, PE masterbatch and film, all PVC applications, PP molding and sheeting		
continued on the next page		

MANUFACTURERS & BRAND NAMES:

J.M. Huber Corporation, Macon, GA, USA

Hubercarb G series (2, 3, 8, 260, 325) milled high brightness grades for paints and coatings

Hubercarb M (6, 4, 3) and S (6, 4) series milled high brightness grades for paints and coatings

Hubercarb Q (325, 6, 4, 3, 2, 1) and W (3, 3N, 4) series milled grades for paints

Milwhite, Inc., Houston, TX, USA

Cal frost MG-NCS dry ground grade for paints, rubber, putties, caulks, adhesives

OMYA/Plüss-Staufer AG, Oftringen, Switzerland

130 companies worldwide producing the large number of grades for different industries under the following brand names:

paper industry: Hydrocarb (slurry), Snowcal (slurry), Omyacarb, Setacarb, Omyafil, Covercarb

paint & coating: Omyacarb, Durcal, Inducarb, Britomya, Snowcal, Calmote, Granitos, Violette

Etikette, Micromya, Omya BSH, Omya BLP, Omyalite, Omya BL, Millicarb, Hydrocarb, Setacarb,

Calibrite, Calcigloss, Calcimatt, Calcicoat (slurry), Wical WS

plastics: Omyacarb, Millicarb, Omyalite, Omya BRL, Omyalene, Omya EXH 1, Britomya,

Snowcal, Omyafoam

rubber and other industries

The available grades in one location are given based on the production in Avenza - Carrara/Italy which manufactures grades of high purity for paints and plastics in one of the oldest and world famous location. The grades manufactured in other locations worldwide have similar quality.

The following grades are produced in Carrara:

Omyacarb 1-AV, 1T-AV, 2-AV, 2T-AV, 5-AV, 10-AV, 15-AV, 30-AV. The number signifies (and it is close to) the mean particle size; the letter T stands for the coated grade

Piqua Materials, Inc., Piqua, OH, USA

Piqua Minerals Filler 30, 60, 70, 200, 300, 600, 1800 - dry ground limestone of particle size increasing with grade number

Polar Minerals, Mt. Vernon, IN, USA

Fine Calcium Carbonates 8102, 8103, 8105, 8107 exceptionally pure calcium carbonates of different particle sizes. Also grades are manufactured with the same number symbol followed by letter C which stands for stearate coated grade

Ultrafine Calcium Carbonates 8.14, 8101 particle size 0.2-1.4 μm produced with (C) and without stearate coating

Polishing Marl - a filler designed to replace diatomaceous earth and calcinated kaolin in automotive and household polishing formulations which improves H&S due to the lack of crystalline silica

Solvay Alkali GmbH, Rheinberg, Germany

Rheinberg Plant - Socal P2, P3, N2R, U1R

Giraud, France - Socal 90A, 92E, BO, 31, 311, 312, 322

Angera, Italy - Socal 90AV, 91CV, 92EV, P2V, 312V, 322V

Ebensee, Austria - Socal P2E, N2, NP, E₂, U₁, U₁S₁, U₁S₂, U₃

the application of grades listed under precipitated grades; pharmaceutical/food grades: P2, U1R, E2, P2V

Suzorite Mica Products, Inc, Boucherville, Canada

Calcium carbonate 80/325 - dry ground limestone

MAJOR PRODUCT APPLICATIONS: *milled grades:* plastics, paper, paints and coatings, and numerous other applications difficult to list due to the widespread use

precipitated grades: emulsion paints, matt paints, paints containing solvent, printing inks, cigarette paper, fine paper, coated paper, special paper, rigid PVC, rubber, PP, PE, polyester, PVC plastisol, PSF, PU, silicone, polyacrylate, filling materials, pharmaceutical preparations, foodstuffs, beverages, toothpaste, wine deacidification, salt after-treatment, welding electrodes, peroxides

MAJOR POLYMER APPLICATIONS: PVC, PE, PP, PS, PA, PSF, PU, silicone, acrylic, rubber, polyester, and many more

Calcium carbonate is the most widely used filler. In the past its use was associated with a substantial cost reduction but today it is the material engineered for the

different requirements of modern products. This discussion begins with an introduction to the origins of calcium carbonate which has been given a thorough evaluation in a paper by Bosshard of Omya/Plüss-Staufer AG.¹³⁸

Calcium at 4.8% is the fifth most common elemental constituent of the earth's crust after oxygen, silicon, aluminum, and iron. It is so popular in practical applications because it is found in rocks and minerals which have very high concentration of calcium carbonate. Calcium carbonate is the most common deposit formed in sedimentary rocks. The process of formation of calcium deposits begins with weathering of land surface due to the changes in heat, frost, rain, and the effect of sun. Calcium carbonate is not readily soluble in water but calcium bicarbonate is. The concentration of carbon dioxide in water is thus important for calcium carbonate transportation from the land to the sea since rain water is the carrier. It is estimated that 500,000,000 tons of minerals are carried by rivers to the seas every year out of which about 10-15% of sedimentary rocks containing calcium carbonate are formed.

The soluble form of calcium can be precipitated in the marine environment to form rock by some physical conditions such as warming of the water (carbon dioxide is less soluble in warm water than in cold water and thus calcium carbonate is precipitated), by the use of carbon dioxide by marine plants, or by alterations in the pH of water by ammonia-producing bacteria which also lowers the solubility of calcium carbonate. However, the majority of calcium carbonate deposits are formed from skeletal fragments of organisms living in the marine environment. Some of these organisms inhabit reefs but the majority float free in water. Figure 2.13 shows various shapes of shells formed by Coccolithophorides which can be spherical coccospheres some, such as dicoaster, are star shaped.¹³⁸

These shells not only have spectacular shapes, but they are small and in abundance. They measure 2-25 μm in diameter and there is up to 35,000,000 cells of coccoliths in a liter of sea water. When they die they sink to the sea bed. It is estimated that 68% calcareous mud covers the bottom of Atlantic. By comparison, only 36% of the Pacific is covered with calcareous mud – the difference is believed to be caused by the differences in solubility of carbon dioxide, and thus of calcium carbonate in the two oceans. When shells or a physically formed precipitate reaches the sea bed, a series of other processes occurs preceding formation of rock. The material loosely deposited on the sea bed contains 80-90% water which is gradually expelled by the overlaying sedimentary matter and the process of lithification takes place. The transformation to rock occurs when the residual porosity attains about 30% which requires a pressure of about 300-500 meters of sediment equivalent to about 80 atmospheres. During this slow process, cementation occurs which is based on redissolving of unstable carbonates such as aragonite or vaterite present in sediments and depositing them in pore spaces as calcite or dolomite. The rocks formed in such a manner are then lifted from the sea bottom in geological upheavals and exposed to weathering to continue the cycle.

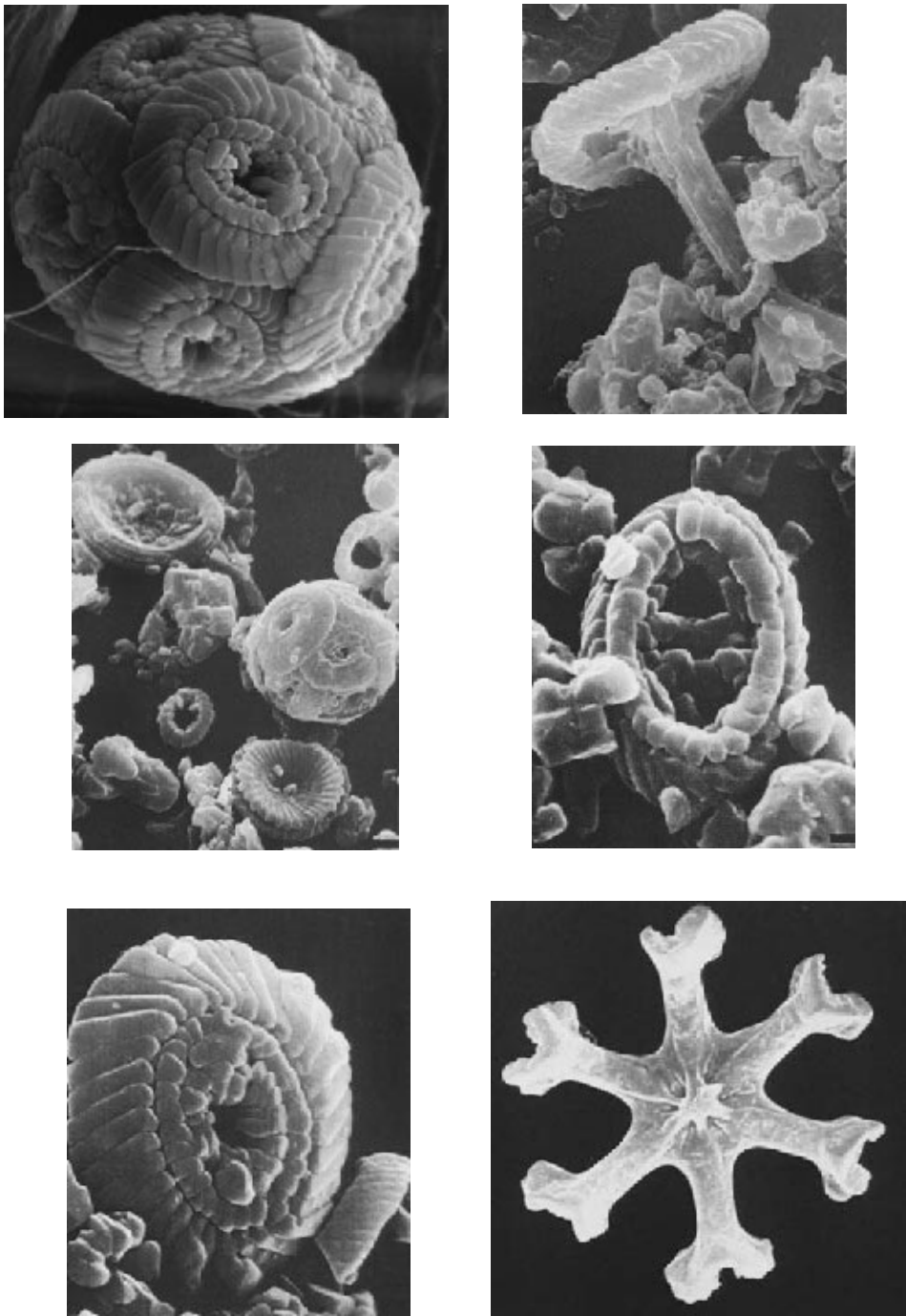


Figure 2.13. Different shapes of coccoliths found in Omya mines. *Courtesy of Omya/Plüss-Stauffer AG.*¹³⁸ The first micrograph (upper left corner) - *Courtesy of ECC International Ltd., St. Austell, UK.*

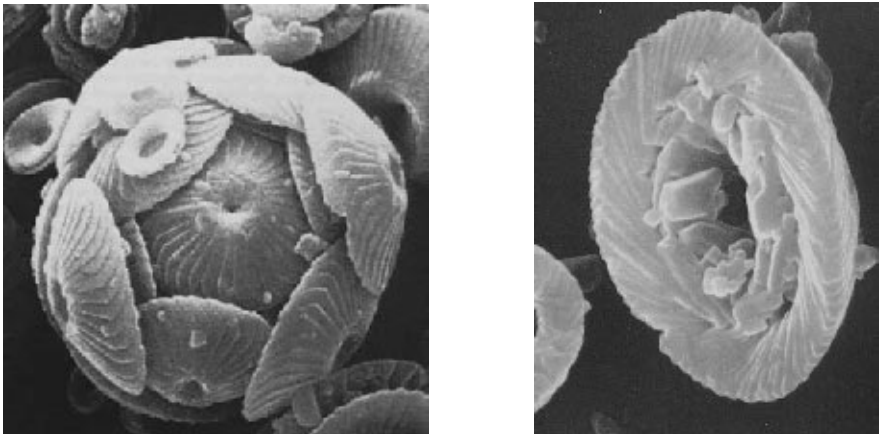


Figure 2.13 (continuation). Different shapes of coccoliths found in Omya mines. *Courtesy of Omya/Plüss-Stauffer AG.*¹³⁸

Most of the concerns about global warming has been for land based plants. It can be seen from the proceeding paragraphs that the oceanic conversion of calcium carbonate by microorganisms and of carbon dioxide by plankton are perhaps more important in the regulation of our environment. Incidents such as an underwater volcanic explosion may affect this balance since they alter the temperature of water and the concentration of carbon dioxide in water and, consequently, its internal use and release to the atmosphere.

As was mentioned before, several crystalline forms can be produced. These forms are used to build minerals and rocks. These are defined below. There are three crystalline forms which are mostly used in production of calcium carbonate filler:

- | | |
|-----------|---|
| calcite | a mineral also called calcspar which has trigonal rhombohedral or trigonal scalenohedral form |
| aragonite | orthorhombic crystals |

Figure 2.14 explains differences between these three forms and compares them with morphology of fillers having these crystalline forms as well as with schematic diagrams of the crystals.

During the biological process of formation, each organism produces a specific crystalline form. For example, the mother-of-pearl or pearl itself are aragonite. Here the prismatic layer is formed of calcite. Aragonite is a less stable form and it can be converted by heating to calcite. Both minerals can be easily distinguished by their physical properties such as density (aragonite 2.9 and calcite 2.7), refractive index (aragonite 1.7, calcite with two refractive indices of 1.49 and 1.66 which

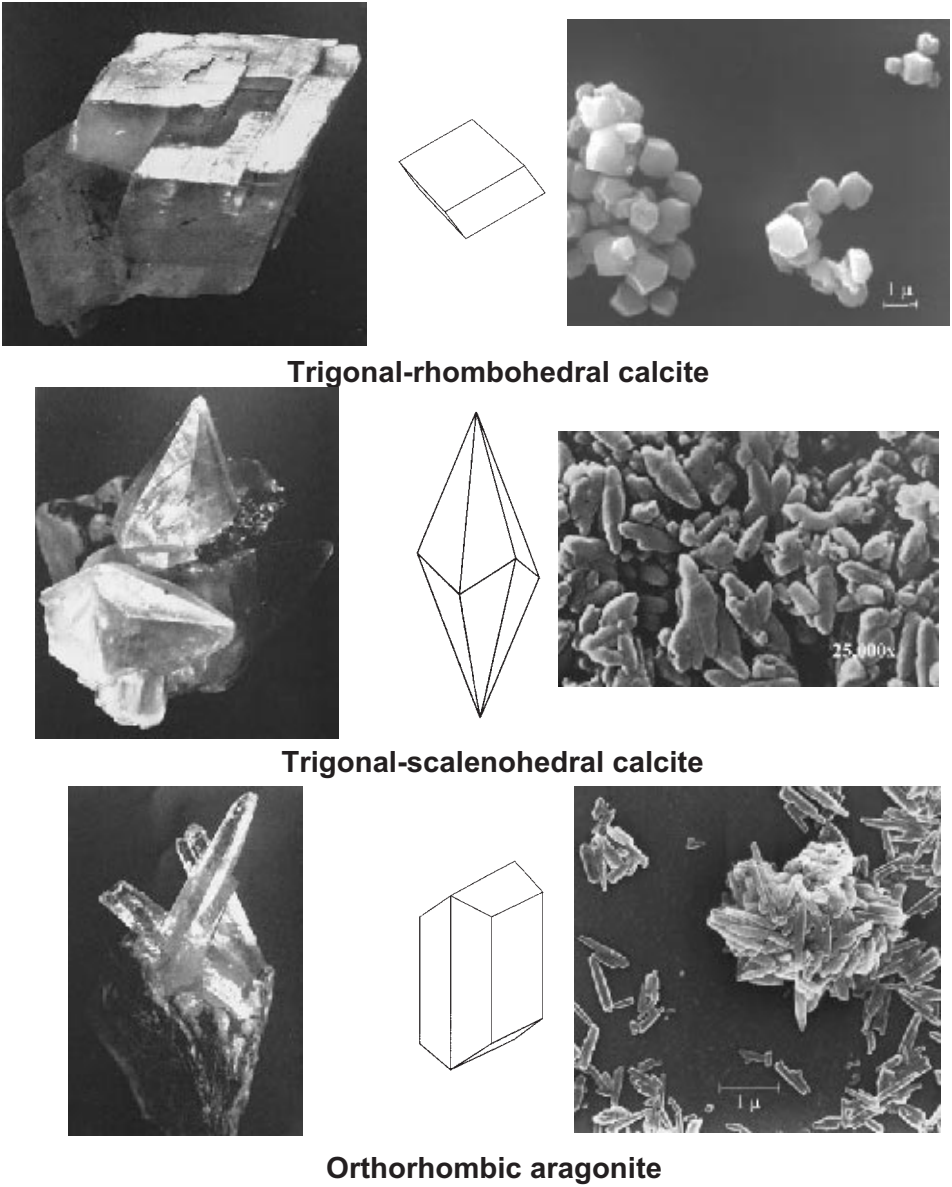


Figure 2.14. Different crystalline forms of calcium carbonate. *Courtesy of Omya/Plüss-Stauffer AG (micrographs of crystals)¹³⁸, Solvay, GmbH, Rheinberg, Germany (crystal structure and micrographs of Socal trigonal-scalenohedral calcite),¹³² and ECC International Ltd., St. Austell, UK (rhombohedral calcite and aragonite).*

causes a double refraction effect), and hardness (aragonite 3.5-4 and calcite 3). There are several other minerals and rocks associated with calcium carbonate:

chalk	a sedimentary rock of soft texture formed from nanofossils
dolomite	mineral composed of calcium magnesium carbonate
limestone	consolidated sedimentary rock
marble	a metamorphic rock originally composed of either calcite, aragonite, or dolomite which was recrystallized to a dense rock under the influence of high pressure and temperature. Its color depends on admixtures (e.g. iron oxide gives yellow to brownish coloration, Carrara marble is white because of high purity)
travertine	deposits from spring water in a form of calcite or aragonite which form in caves dripstones (stalactites and stalagmites)
vaterite	a hexagonal modification of calcium carbonate which is very unstable and it is readily converted to calcite

The above review of rock and mineral formation indicates that all calcium carbonates are not the same. Their type and properties depend on their history of formation. In addition to the above processes of formation, the presence of admixtures also determines the process used to extract or refine the filler and its utility. Other minerals such as silicates and clays are formed simultaneously and within calcium carbonate and altogether they form a broad range of mixtures which must be processed. This aspect of the production is underlined in recognition that it is very important for a final product process to use a particular grade of material dependent on the technology of production and the place of origin.

Three major technological processes are used in the production of calcium carbonate filler. These are milling, precipitation, and coating. More than 90% calcium carbonate is processed by milling. Two methods are used: dry and wet. The milling technology was developed for reproducibility and to obtain the required particle size distribution. In addition to general grades, ultrafine grades are also produced by the milling process. If the wet milling process is used, the material is frequently delivered to the customer in the form of a slurry which makes subsequent processes more economical and environmentally friendly. The paper industry uses about 80% of its calcium carbonate in the form of slurry. Also, paints use large quantities of slurried calcium carbonate. Figure 2.15 shows SEM micrograph of milled calcium carbonate. In this process, the crystalline structure of the rock has an important influence on the morphology of the filler.

Figure 2.16 shows a schematic diagram of the production of precipitated calcium carbonate. Such grades are also termed synthetic calcium carbonate since several chemical operations are performed. The first operation is calcination which is performed in a kiln at 900°C. At this stage, calcium carbonate is decomposed to

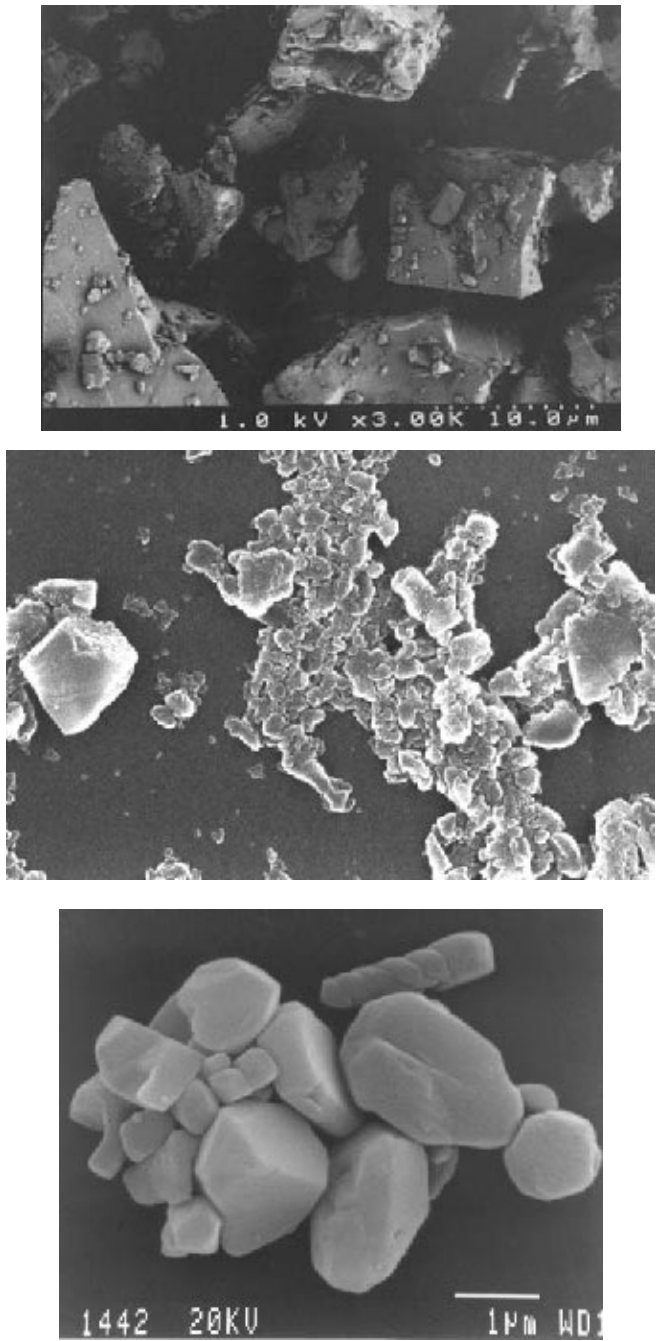


Figure 2.15. SEM of different calcium carbonates. upper - milled calcium carbonate, middle - ultrafine ground calcium carbonate, bottom - chalk. *Courtesy of J.M. Huber Corporation, Macon, GA, USA (upper), and ECC International Ltd., St. Austell, UK (middle and bottom).*

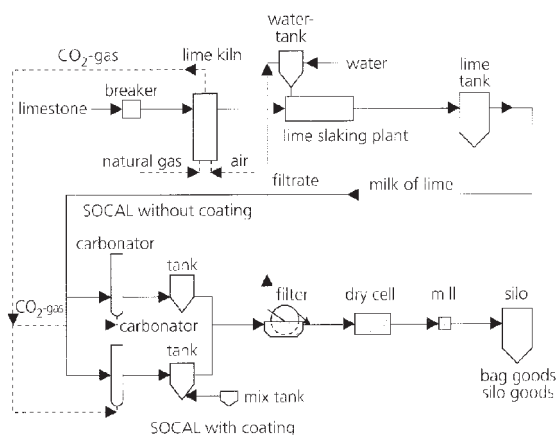


Figure 2.16. Schematic diagram showing the production of precipitated calcium carbonate. *Courtesy of Solvay GmbH, Rheinberg, Germany.*

calcium oxide and carbon dioxide which is used in further step. In the next step, calcium oxide is mixed with water in a process called slaking. This converts calcium oxide to lime and permits a material purification operation to be performed which results in a product of improved purity. In the (sometimes) final operation, the milk of lime is saturated by carbon dioxide which precipitates calcium carbonate. Depending on process parameters such as temperature, degree of purification, and concentration of reagents, different grades are produced which can be distinguished by particle size distribution, or crystalline form, or may be graded for food or pharmaceutical use (Figure 2.14). One additional operation is surface coating during which a 1-3 wt% coating is deposited on the surface of calcium carbonate particles. In most cases, salts of fatty acids are used for coating but titanates and zirconates are also used although less frequently. Grafting various polymers onto the surface is the subject of current research. Rhombohedral calcite is the most likely to be coated. Because of coating its particles do not agglomerate and become hydrophobic. Aragonite or calcite scalenohedral form is likely to be used if calcium carbonate must play the role of a secondary pigment. Here, higher light scattering and brightness are obtained by forming some aggregation. Scanning electron micrographs show that the surface coating, by itself, does not introduce any particular morphological features.

There are also special morphological grades of calcium carbonate which can be used to change the rheological characteristics of materials. One example of such a product is shown in Figure 2.17. The combination of particulates and elongated particles creates special rheological effects. In addition, the elongated particles are

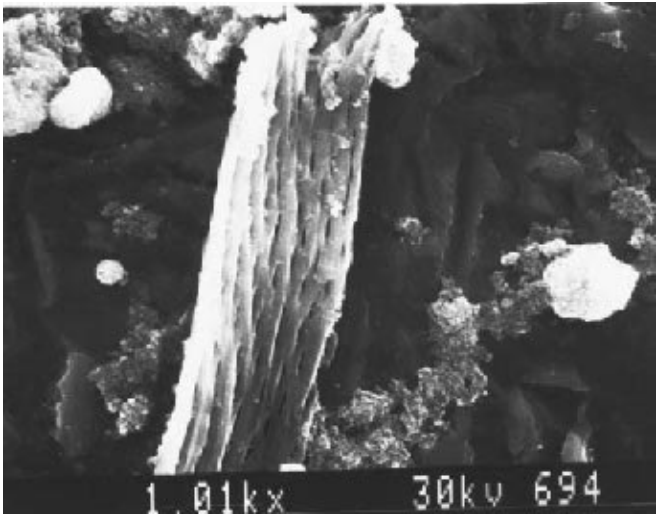


Figure 2.17. SEM micrograph of Viscolite U.

covered by a system of microcracks which contribute to non-Newtonian rheological characteristics which this filler imparts.

2.1.20 CALCIUM HYDROXIDE

Names: calcium hydroxide, carbide lime, lime hydrate, hydrated lime, slaked lime		CAS #: 1305-62-0
Chemical formula: Ca(OH) ₂	Functionality: OH	
Chemical composition: Ca(OH) ₂ - 80-90%, CaCO ₃ - 10-20%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.2-2.35	Melting point, °C: 272	
CHEMICAL PROPERTIES		
Chemical resistance: not resistant to strong acid, phosphorus, maleic anhydride		
Moisture content, %: 1.5	pH of water suspension: 11.4-12.6	
OPTICAL PROPERTIES		
Refractive index: 1.57	Color: gray	
MORPHOLOGY		
Particle shape: round	Crystal structure: hexagonal	Particle size, μm: 5
Specific surface area, m ² /g: 1-6		
MANUFACTURER & BRAND NAME: ReBase Products, Inc., Barrie, Canada White Knight 100 - acetylene production co-product derived from carbide lime		
MAJOR PRODUCT APPLICATIONS: similar to calcium carbonate		
MAJOR POLYMER APPLICATIONS: PVC and PE already use the product		

Calcium hydroxide is a product new to the market. There have been, in past, positive scientific reports of its usefulness. The benefits of calcium hydroxide over calcium carbonate are its functionality, particle shape (more spherical and thus less abrasive to the equipment) (Figure 2.18), its lower density (decreases the density of product and lowers the price), a refractive index closer to many polymers, and its lower cost (approximately half of the price of calcium carbonate). The manufacturing equipment includes an excitement chamber, metered conveying, pneumatic transportation, flash drying, classification, and silo storage. The manufacturer delivers product to customers by its own silo-trucks.

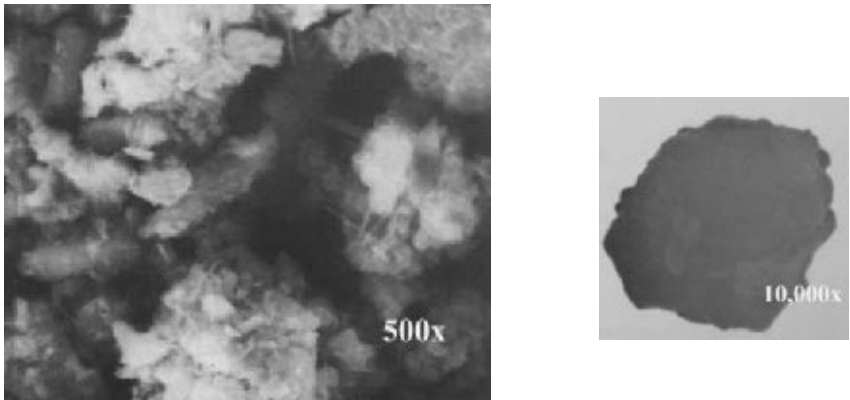


Figure 2.18. SEM micrograph of White Knight 100 calcium hydroxide particle. *Courtesy of ReBase, Barrie, Canada.*

2.1.21. CALCIUM SULFATE

Names: calcium sulfate, gypsum, anhydride		CAS #: 7778-18-9 or 10101-41-4 (dihydrate)
Chemical formula: CaSO ₄ , CaSO ₄ ·2H ₂ O		Functionality: none
Chemical composition: CaSO ₄ - 98.7-99%, SiO ₂ - 0.31% (dihydrate contains CaSO ₄ ·2H ₂ O - 82.3% and CaCO ₃ ·MgCO ₃ - 12.2%)		
Trace elements: Fe, heavy metals - ppm quantities		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.3-3	Mohs hardness: 2	Melting point, °C: 1450
Decomposition temp., °C: 128-63	Maximum temperature of use, °C: 128	
CHEMICAL PROPERTIES		
Chemical resistance: reacts with strong mineral acids		
Moisture content, %: 0.1	pH of water suspension: 6.8-10.8	
OPTICAL PROPERTIES		
Refractive index: 1.52-1.61	Color: white to light gray	
MORPHOLOGY		
Crystal structure: monoclinic	Cleavage: one direction	
MANUFACTURERS & BRAND NAMES: Charles B. Chrystal Co., Inc., New York, USA Terra Alba USP Granulated & English - pure forms for pharmaceutical industry NF Grade - calcinated terra alba for food and pharmaceutical industries LP #2 - dihydrate for filling and fire retarding applications 204 - anhydrous grade for TiO ₂ replacement and drying agent		
MAJOR PRODUCT APPLICATIONS: pharmaceutical, food, plastics, paints		
MAJOR POLYMER APPLICATIONS: polyester, PU, PVC		

Gypsum shows very little variation in chemical composition, and it is the most common of the sulfate minerals. Its origin is related to a high concentration in sea water (4%) from which it is deposited by sedimentation or evaporation. The last mode of formation may also result in anhydrite formation because both forms are metastable and exist in equilibrium conditions.

The hydrous form of calcium sulfate, *Terra Alba*, contains about 20% water of crystallization. It is processed by fine grinding and air-separation to a selected, white, high purity gypsum. The anhydrous gypsum form is obtained by the same process, the addition of a calcination step in which water is almost entirely removed (only about 0.3% remains). Particles are mostly smaller than 10 μm. Oil absorption is rather high, in the range of 23 to 26 g/100 g. The choice between the hydrous and the anhydrous forms depends on the processing temperature and the moisture sensitivity of the formulation.

Color is another important consideration. Anhydrous forms are brighter than the hydrous ones because of their crystalline form, particle size, and purification during the calcination process. Particle size distribution depends mostly on the grinding process. *Terra Alba*, made by fine grinding and air-separation, has an average particle size of 12 μm , whereas anhydrous calcium sulfate has an average particle size of 7 μm . A fine grinding yields a product with an average particle size equal to 1.4 μm .

MANUFACTURERS & BRAND NAMES:

Degussa Corporation, Akron, OH, USA

Corax N110, N220, N234, N299, N326, N330, N339, N347, N550, N650, N660, N754, N762, N774
all furnace blacks

Carbon, Brussels, Belgium, distributed by R.T. Vanderbilt Company, Inc., Norwalk, CT, USA

Ensaco 150, 200, 250 - carbon black produced in form of powder and granules in process similar to furnace black but differing in aerodynamic and thermodynamic conditions. No water quenching is used in the process. The resultant material is closer to acetylene black than furnace black. Unique properties of this carbon black are utilized in dry-cell batteries, paint, plastics, and rubber markets.

Sid Richardson Carbon Black Company, Fort Worth, TX, USA

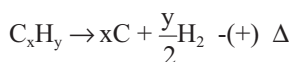
MAJOR PRODUCT APPLICATIONS: tires, plastics, inks, paints, and many other

MAJOR POLYMER APPLICATIONS: most polymers and rubbers

Carbon black, initially used as pigment in ink, has the longest history of all the materials discussed in this book. It was produced in China about 3000 B.C. and exported to Japan around 500 A.D. But only in the last 50 years has the technological development in both carbon black production and processing of rubber and polymers resulted in the tremendous variety of products which we know today.

Structurally, carbon black is similar to graphite, composed of large sheets of hexagonal rings formed by carbon atoms separated from each other by a distance of 0.142 nm (i.e., close to the length of the C-C bond in benzene – 0.139 nm). The values of 0.148, 0.134, and 0.12 nm are usually assigned to the single, double, and triple bond distances between two carbons, respectively. This means that the bond length in graphite is between the length of a single and a double bond. The bond length in carbon blacks is also 0.142 nm and hexagonal rings form large sheets, as in the case of graphite. The difference between the graphite and carbon black is in the arrangement of layers. In the case of graphite, the layers are stacked on each other regularly in such manner that each carbon atom has directly above and below it another carbon atom, meaning that the structure has a tri-dimensional order. The distance between carbon atoms in each layer is 0.335 nm. The layers of carbon blacks are also parallel to each other but not arranged in order, usually forming concentric inner layers. Such an arrangement is called a turbostratic structure. The separation distance between parallel layers of carbon blacks varies in the range of 0.350-0.365 nm. The interior of carbon black aggregate is less ordered than its surface and that is why it is chemically more reactive, as confirmed by oxidation studies. Carbon black exposed to high temperature undergoes a graphitization process. Oxygen present in the system reacts with the carbon atoms in the center of particles, resulting in formation of hollow spheres having an increased crystallinity. From what has been said so far, it is not surprising that carbon black has low crystallinity and, in fact, is regarded as amorphous carbon having a degenerated graphitic structure.

The basic reaction of carbon black formation is as follows:



Therefore, hydrocarbon-containing materials have the potential to be used in carbon black production. Raw materials can be in the form of hydrocarbon gases, such as methane and acetylene, but mostly viscous residual aromatic hydrocarbons are used. Depending on chemical composition, the reaction is exo- or endothermic. Only when carbon black is produced from acetylene the reaction is exothermic and the process demands intensive cooling, whereas in other cases the reaction is endothermic and needs a substantial amount of energy in order to form carbon black.

Several methods can be used for the production of carbon black. The Lampblack Process, the oldest of all, was developed by the Chinese. Initially, vegetable oil was burned in small lamps with tile covers to accumulate the carbon black formed. Later, shallow pans were used in systems with a restricted air supply. Carbon black in this process was recovered from smoke in settling chambers. This method is still used for production of small quantities of carbon black. The Channel Black Process is another method useful in the past and not important for present production. Natural gas is used as a raw material in this process; it is burned in close proximity to steel channels on which carbon black is deposited. Carbon black is removed from the channels by scrapers and falls into hoppers beneath the channels. This process was discontinued in the USA in 1976 because of the price of natural gas, smoke pollution, and low yield. It is still being used in Germany, Eastern Europe, and Japan.

The Thermal Decomposition Process and the Acetylene Black Process are similar in the sense that both processes are conducted in the absence of air and flame, and both use gaseous raw materials. In the Thermal Decomposition Process, natural gas is fed into a generator having a temperature of 1300°C where it undergoes cracking. A stream of product gases, containing carbon black, hydrogen, methane, and other hydrocarbons, is cooled with water sprays and carbon black is removed by bag filters. The process is cyclic in nature because the endothermic reaction requires heating of the generator at 5 minutes intervals. In order to achieve a continuous process, two generators work together in 5 minutes cycles. When one generator is producing, the other is heated, partially by product gases having a high calorific value. A similar process is performed in England with the use of oil, which performs two roles: heating material and raw material for carbon black production. The Acetylene Black Process involves burning the acetylene in a metal retort to attain the process temperature (800-1000°C), then the process is continued in an oxygen-free atmosphere, while heat produced by the exothermic reaction is taken away by a water cooling system. The process gives a product of very low density, which is difficult to compress and resistant to pelletization.

The Oil-Furnace Process is by far the most prevalent method of carbon black production. It is a further development of the Gas Furnace Process. A reactor is fed by liquid hydrocarbon feedstock which is injected, atomized, and mixed with preheated air and auxiliary fuel (usually natural gas). Part of the feedstock is used to maintain the reaction temperature (1450-1800°C) and the remainder is converted to

carbon black. The reaction is quenched with water spray and the carbon black is separated from the combustion gases by bag filters and cyclones. The process is completed by pelletizing and drying. An Oil-Furnace Process line is usually equipped with a computer-control system because process conditions greatly affect the product properties.

The installations used in this process are usually very large and they are equipped with energy-saving systems. In the early 1970s, reactor and burner designs were improved, resulting in better mixing and atomization, and lower residence times. A series of new types of carbon blacks was introduced, called “New Technology” or “Improved” carbon blacks. This new development yields products of narrower distribution of aggregate sizes, higher surface activity (higher bound rubber and higher moisture absorption), and more open aggregates (branched, bulky).

The Oil-Furnace Process has superior efficiency and economy. It is also the most versatile process, allowing production of most grades important for industry. Table 2.1 outlines differences between carbon blacks manufactured in five processes.

Table 2.1. Typical properties of carbon blacks manufactured in different processes.

	Furnace	Thermal	Acetylene	Channel	Lamp
	HAF	MT		EPC	Lb
	N-330	N-990		S300	
Av. particle diameter, nm	28	250	40	28	65
BET surface area, m ² /g	75	7-12	65	115	22
DBP absorption, ml/100 g	103	44	250	100	130
Tinting strength, %SRF	210	35	108	180	90
Toluene extract, %	0.06	0.5	0.1	0.0	0.2
pH	7.5	9-11	4.8	3.8	3.0
Volatile material, %	1.0	0.1	0.3	5.0	1.5
Ash, %	0.4	0.2	0.0	0.02	0.02
Composition, %					
C	97.9	99.6	99.7	95.6	98.0
H	0.4	0.2	0.1	0.6	0.2
S	0.6	0.01	0.02	0.2	0.8
O	0.7	0.1	0.2	3.5	0.8
Raw material	oil or gas	gas	acetylene	gas	coal tar
Yield, % theor.carbon	23-70	30-45		1.6-6.0	
Energy use, J/kg	9.3-16x10 ⁷	2.0-2.8x10 ⁸		1.2-2.3x10 ⁹	

Acetylene blacks are the purest products manufactured, whereas in the thermal process one can obtain carbon black of the lowest surface area. Channel carbon blacks are surface oxidized as a result of their exposure to air at elevated temperatures. Particles of channel blacks are slightly porous, and the high level of surface oxidation may retard vulcanization rate, but when it is used in polyethylene it improves weathering resistance because the phenol and hydroquinone surface groups have antioxidant properties. A high level of sulfur in oil-furnace blacks depends on the composition of feedstock and can be reduced by its proper choice. It is important in this process that raw materials also contain low levels of alkali metals which affect the size of aggregates. Aromaticity of feedstock increases the degree of aggregation, while injection of alkali metal decreases it. One should not be misguided by the results quoted in Table 2.1, which contains data on particular grades but does not reflect their full variety. For example, Oil-Furnace Process blacks have a specific surface area in the range of 25-560 m²/g, particle size from 13 to 75 nm, and carbon content from 90.5 to 98%. Although carbon blacks are produced by various manufacturers according to the standards set by industries, differences exist and the evaluation of products based on a simple comparison of results of their analysis cannot contribute to a reliable technology; therefore their performance should be evaluated during product formulation.

Such a great number of carbon blacks is now manufactured by the industry that without the help of an adequate classification it will be difficult to search for a product that may serve a particular purpose for a carbon black application. Before the Oil-Furnace Process was fully applied, classification was based on both the process of production and the properties of carbon black. Later, the Oil-Furnace Process took some markets from other processes and developed products of similar properties. This practically ruined the former classification (process type became unimportant) and a need for a new classification became apparent. A new classification is based on one letter and three digits (Table 2.2). The letter is N (for normal) and S (for slow), which describes the effect of carbon black on the rate of cure in rubber processing. The first digit refers to the average particle size, as specified in the ASTM Standard. The lower the digit, the smaller particle size; for example, 1 means particle size between 11 and 19 nm, whereas 9 means average particle diameter between 201 and 500 nm. The last two digits are assigned arbitrarily and characterize the set of several properties of carbon blacks, such as iodine adsorption, pour density, etc., which are typical for a particular grade. There is no particular relationship between the last two digits and carbon black properties that can be put in a logical order.

The ASTM classification provides some information about the carbon black type, but the information still can be broadened if one also uses the old classification along with it, and that is why both classifications are frequently used.

The conversion from an old to a new system is not always precise as far as particle size diameter is concerned, but knowing the old designation helps to

establish such characteristics as abrasion resistance, reinforcement level, vulcanizate properties, processing properties, typical application, particle size, and electric conductivity. Many designations used in the past were dropped from use because they were related to particular processes which are not used frequently now, such as lampblack (LB), medium flow channel (MFC), etc. When properties are discussed in more detail, we learn that neither classification is sufficient for choosing carbon black arbitrarily, which should be quite obvious, taking into consideration the amount of produced grades and the sophistication of present technology.

Table 2.2. Carbon black classification

ASTM N-type	Designation
N100 to N199	super abrasion furnace, SAF
N200 to N299	high aggregate furnace
N300 to N399	intermediate super abrasion furnace, ISAF
N400 to N499	fine furnace, FF, and conductive furnace, XCF
N500 to N599	fast extrusion furnace, FEF
N600 to N699	high modulus furnace, HMF, general purpose furnace, GPF, and all-purpose furnace, APF
N700 to N799	semi-reinforcing furnace, SFR
N800	fine thermal, FT
N907	medium thermal non-staining, MT-NS
N990	medium thermal, MT

Let us now discuss the physical properties of carbon blacks currently available in the market. Particle and aggregate size are probably the most important factors characterizing carbon blacks. In order to understand them fully, one should consider the mechanism of carbon black formation. In the Oil-Furnace Process, liquid raw material is atomized in a furnace having a very high temperature. Formation of carbon black is a gradual process in which a few phases can be singled out: droplet vaporization, molecular rearrangement, and decomposition. During molecular rearrangement, large polyaromatic molecules are formed which gradually lose hydrogen and finally become almost pure carbon. It is easy to imagine that such transitions have to be accompanied by a gradual change of state from a liquid to a solid through a viscous state. As long as particles are in the form of liquid droplets, they can easily combine to form larger droplets or disintegrate to smaller ones, depending on the mixing degree and time-temperature relationship of a liquid state. Generally, we can say that during the stage of liquid state, primary particles are formed and their size depends on the process parameters. Viscosity

increases with loss of hydrogen and the formation of spherical particles becomes more difficult, but colliding particles may adhere to each other since they are in a viscous state, and partial fusion may occur. This period regulates the size of the aggregates formed, meaning the number and spatial distribution of primary particles forming an agglomerate. As decomposition progresses, aggregates finally reach a stage at which they become solid and can no longer adhere to each other to form durable fusion points. The only way by which the size of an aggregate can increase after this stage is by weak attractive forces that are easy to disrupt during carbon black compounding. When agglomerates are formed, they should not be exposed to the high process temperature since they may undergo crystalline changes known as graphitization. That is why carbon blacks are water-quenched. If water quenching is done too early, it results in carbon black containing an increased amount of tar.

Figures 2.19 and 2.20 show the difference between low structure and high structure carbon blacks.

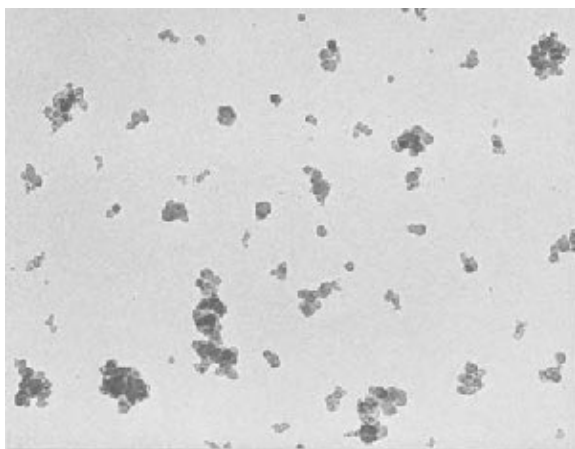


Figure 2.19. TEM micrograph of carbon black N326 (low structure). *Courtesy of Columbian Chemicals Company.*

The above mechanism clearly shows that by varying the process parameters, one can easily regulate the size of the primary particles and the structure of agglomerates. Although the average particle diameter is the basis of the ASTM classification of carbon blacks in processing technology, this factor is usually not used due to technical difficulties with measurement. Particle diameter can be measured by electron microscopy and it is therefore difficult to obtain accurate values for a representative sample size. The use of an image analyzer did not solve this problem. The surface area of carbon black is the most useful parameter relating to particle size and agglomerate size. Several methods are used for this measurement – the simplest, iodine number measurement, is a fast and a precise

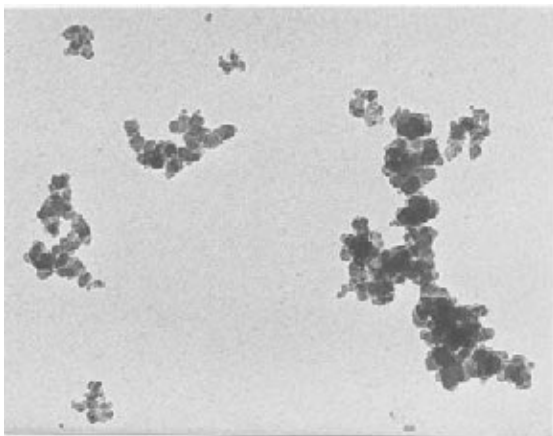


Figure 2.20. TEM micrograph of carbon black N326 (high structure). *Courtesy of Columbian Chemicals Company.*

method, but results are affected by the presence of residual extractable materials and surface oxygen. The BET method is an exact and valuable tool for fast and accurate measurements. The porosity of carbon blacks can be estimated from the difference between the result of the BET method and adsorption of large molecules like cetyltrimethylammonium bromide from aqueous solution. Similar results can be obtained by the so-called ' t' ' method, based on the BET principle with the use of controlled conditions of adsorption and a standard sample for comparison. In most grades of carbon black, the porosity is rather low, and a higher porosity usually shows that carbon black was oxidized.

For non-porous particles, the average particle diameter can be closely estimated from the specific surface area since the two values are inversely proportional to one another. Although many efforts have been made to analyze particle size distribution, the size of the particle has only a secondary effect on the size and structure of the aggregate. The reason is that the primary particles are strongly connected in the aggregates and even the most abrasive processing methods do not affect the structure of aggregates. Only up to one fracture per aggregate occurs in rubber processing. This is the primary reason that many efforts have been made to evaluate the structure of aggregates. Three main possibilities exist in the determination of aggregate size and structure:

- Electron microscopy
- Centrifugal sedimentation
- Liquid absorption.

Electron microscopy allows one to analyze the average particle size, the number of particles per agglomerate, and the projected area from which a calculation of the void volume of each aggregate can be done. Centrifugal sedimentation allows direct measurement of the size distribution of aggregates

larger than a certain Stokes diameter. The major problem with this method is related to incomplete dispersion and flocculation of aggregates. Finally, the liquid absorption (usually of dibutyl phthalate) gives the void volume in aggregates directly.

Carbon black structure affects the physico-mechanical properties of the material, such as tensile strength, elongation, water absorption, tinting strength, die swell, etc., which are discussed under their respective topics in Chapter 5.

Let us now examine practical examples of carbon blacks chosen from the range of products of the Cabot Corporation, which were selected to show a variety of carbon blacks in respect to their structure and particle size (Table 2.3). Table 2.3 shows that because each carbon black differs in particle size, particle porosity, and aggregate structure, the relationship between parameters cannot have a high correlation.

Table 2.3. Surface area, particle size and oil absorption of some Cabot grades

Type	Surface area, m ² /g	Particle size, nm	Oil absorption, g/100 g
Black Pearls 2000	1475	15	300
Black Pearls 1300	560	13	105
Black Pearls 1100	240	14	50
Vulcan 9 A32	140	19	114
Regal 300 I	80	27	72
Sterling SO	42	41	120
Sterling NS	25	75	70

The morphology of carbon black and, in particular, the presence of agglomerates makes it difficult to process. The chemistry of carbon black and, particularly, the chemistry of its surface must be considered in selecting carbon black for a particular application and in determining the best processing method. Heat treatment of carbon black produces both physical and chemical changes in surface activity. Oxygen is usually reacted before the temperature reaches 1000°C, whereas the hydrogen is gradually removed in the temperature range 800 to 1600°C. It is known that oxygen in carbon blacks forms carboxyl, quinone, lactone, and phenolic groups, and they are lost on heating to 950°C. This loss is the volatile content of carbon black. The presence of active groups on the surface of carbon black facilitates wetting, dispersion, and adsorption of moisture. These factors, in turn, increase the reinforcing effect and facilitate dispersability of carbon blacks. Volatile content varies in the range of 0.5 to 11% and the reinforcing types of carbon blacks usually have 2-3% of volatiles. Properties of carbon blacks should also be analyzed for the presence of organic residue, given by the amount extracted

by solvents. The organic residue, which is a tar-like product, can migrate to the surface in the compounded product and cause staining.

Research on carbon black continues and the most important topics remain its structure, the effect of functional groups on carbon black properties, the effect of the measured parameters of carbon black on its performance in various systems, and the influence of processing parameters on the product. These and other influences are discussed throughout the book.

2.1.23 CERAMIC BEADS²⁴⁴⁻²⁴⁷

Names: ceramic beads, ceramic spheres, microspheres		
Chemical formula: n/a		Functionality: OH, silane treatment
Chemical composition: silica alumina ceramic, alkali alumino silicate ceramic; SiO ₂ - 55-65%, Al ₂ O ₃ - 25-38%, Fe ₂ O ₃ - 0.5-5%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 0.24-2.5	Mohs hardness: 5-7	Softening point, °C: 980-1400
Thermal conductivity, W/K · m: 0.23	Compressive strength, MPa: 1-34 (hollow), 400 (solid)	
CHEMICAL PROPERTIES		
Chemical resistance: high chemical resistance		
Moisture content, %: 0.2-0.5	pH of water suspension: 4-8	
OPTICAL & ELECTRICAL PROPERTIES		
Color: white, off-white, gray	Conductance, mhos/cm: 200	Dielectric constant: 1.6
MORPHOLOGY		
Particle shape: spherical	Particle size, µm: 50-350 (hollow), 1-200 (solid)	
Shell thickness: 10% diameter	Specific surface area, m ² /g: 0.1-1.1	
Sieve analysis: residue on 325 mesh sieve - 0.01-26%		Hegman fineness: 3-7
MANUFACTURERS & BRAND NAMES: Kinetico Incorporated Macrolite Ceramic Spheres ML 535, 357, 714, 1430, 3050 PQ Corporation, Valley Forge, PA, USA Extendspheres SG standard grade of hollow spheres Extendspheres CG medium size hollows spheres Extendspheres TG smaller size hollow spheres Extendspheres XOL-200 smallest diameter hollow spheres Sphere Services Inc., The Cenosphere Company, Oak Ridge, TN, USA Recyclospheres - ceramic hollow microspheres manufactured from fly ash in three particle size ranges with maximum diameter of 150, 210 and 300 µm Bionic Bubble - ceramic hollow microspheres manufactured from fly ash in three particle size ranges with maximum diameter of 75, 100 and 125 µm Zeelan Industries, Inc., wholly-owned subsidiary of 3M, St. Paul, MN, USA Z-light Microspheres G-3400, G-3500, W-1000, W-1012, W-1100, W-1200, W-1300, W-1600 hollow microspheres differing in color (G - gray, W - off-white) and particle size Zeospheres G-200, G-400, G-600, G-800, G-850, W-210, W-410, W-610 solid microspheres differing in color (G - gray, W - white) and particle size		
MAJOR PRODUCT APPLICATIONS: <i>hollow</i> : bowling balls, cultured marble, plywood patch, roof coatings, refractory materials, grinding wheels, lightweight cement, polymer concrete, exterior insulating finishes, synthetic stucco, asphalt repair compounds, automotive sealants, roofing tiles, carpet backing, chemical resistant coatings, adhesives, sealants, pipe insulation, paint stripper, PVC flooring <i>porous</i> : plastic molds, paints, coatings, sealants, asphalt, rubber, boat construction and repair, lightweight concrete, gypsum wall board, catalyst support, stucco, energy absorbing filler for autobody parts <i>solid</i> : industrial paints, film antiblock, powder coatings, maintenance paints, adhesives, polymer concrete, textured coatings, house paints, low gloss paints, decorative flooring		

MAJOR POLYMER APPLICATIONS: PP, PE, PS, PA, PVC, PPS, TFE, polyesters, epoxy, polyurethanes, phenolic, silicones

Ceramic spheres are produced from nepheline syenite, aluminum oxide, and bentonite or fly ash. Ceramic spheres have substantially higher densities than glass or polymer beads but are less expensive, more rigid and mechanically resistant due to their thicker walls. They have strength of all spherical materials which give the highest packing density and they improve flow because of the ball-bearing effect. In addition, ceramic spheres reduce dielectric constant, warpage, shrinkage, and improve crack resistance of speckling compounds.

A simple formula allows us to calculate the amount of beads required to replace a filler of higher density: Amount of beads = (density of beads/density of filler) \times amount of filler in composition. Considering that beads have a better packing density than the filler they are replacing and produce a lower viscosity in the material, more beads can be added than is calculated from equation and yet maintain the same viscosity in the material. Although ceramic spheres are more rigid than glass spheres, they still require special precautions during handling and mixing. A high shear and prolonged mixing should be avoided during their incorporation. Ceramic beads should be added at the end of the mixing process.

Figure 2.21 shows the morphology of ceramic beads which are composed of a mixture of spherical particles. The unique beads produced by Kinetico have a denser shell to give them more mechanical strength and a porous interior to reduce their density (Figure 2.22).

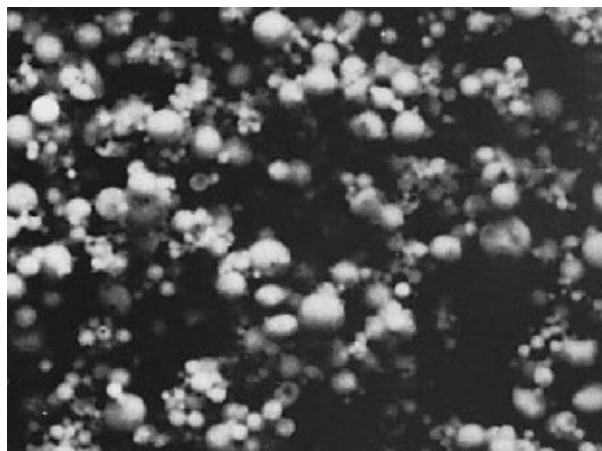


Figure 2.21. SEM micrograph of Zeeospheres. *Courtesy of 3M, St. Paul, MN, USA.*

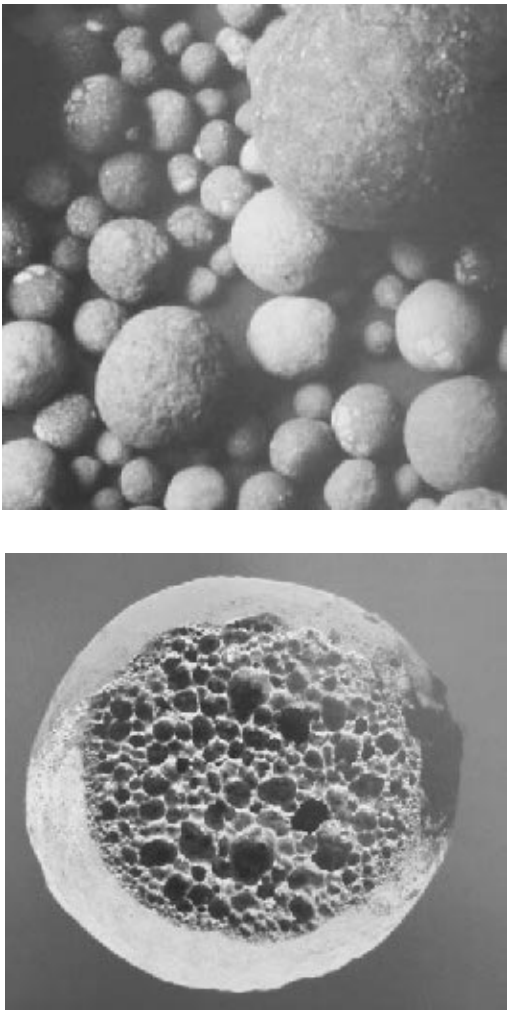


Figure 2.22. SEM micrograph of Macrolite – choice of sizes (upper) and cross-section (lower). *Courtesy of Kinetico, Inc., Newbury, OH, USA.*

2.1.24 CLAY²⁴⁸⁻²⁵³

Names: clay, ball clay		CAS #: 1332-58-7
Chemical formula: composition variable		Functionality: OH
Chemical composition: SiO ₂ - 53.3-61.2%, Al ₂ O ₃ - 24.3-32.5%, Fe ₂ O ₃ - 1.2-1.7%, TiO ₂ , - 1-1.1%, CaO - 0.2-0.3%, MgO - 0.2-0.4%, K ₂ O - 0.3-1.3%, Na ₂ O - 0.1-0.3%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.6	Mohs hardness: 2-2.5	Loss on ignition, %: 9.5-12.6
CHEMICAL PROPERTIES		
Chemical resistance: reactive with acids and alkalis		
Moisture content, %: 3	Adsorbed moisture, %: 5.5-14.5	pH of water suspension: 3.9-9
OPTICAL PROPERTIES		
Color: white, tan, gray		Brightness: 60-64
MORPHOLOGY		
Particle size, μm: 0.4-5	Oil absorption, g/100 g: 36-40	
Sieve analysis: 325 mesh residue 1.6-2.2%	Specific surface area, m ² /g: 18.9-30.5	
MANUFACTURERS & BRAND NAMES: ECC International, St. Austell, UK Hexafil and Hexafort H - ball clays for plastic and rubber Kentucky-Tennessee Clay Company, Langley, SC, USA #3380, Tenn #6 for rubber compounds, adhesives, plastics and other applications. In addition, the company manufactures a large number of grades for ceramics in Mayfield, KY and Gleason, TN Old Hickory Clay Company, Hickory, KY, USA manufacturer of large number of ball clay grades. No. 5 grade is used as filler in paints and plastics United Clays, Brentwood, TN, USA manufacturer and importer of clays from around the world (China, France, Germany, Indonesia, Thailand, UK, Ukraine)		
MAJOR PRODUCT APPLICATIONS: rubber, adhesives, protective coatings, traffic paint, joint compounds, plastics, cables, belting, footwear, plant lining, tires		
MAJOR POLYMER APPLICATIONS: PVC, rubber, urea formaldehyde, phenol formaldehyde		

Popularly-known fillers, such as kaolin clay, China clay, bentonite, Fuller's earth, and vermiculite all are clay minerals. Clay minerals are divided into 5 groups. The kaolinite group includes kaolinite and halloysite; the illite group includes illite; the smectite group includes montmorillonite and hectorite; the palygorskite group includes sepiolite and attapulgite, which, with vermiculite, are precursors of clay fillers. Kaolinites were formed by hydrothermal alteration or weathering of feldspars, and other silicates. Acid conditions favor kaolinite formation, whereas alkaline conditions favor formation of smectites. Both minerals are often accompanied by quartz, iron oxides, mica, and pyrite. The chemical composition of kaolinite is subject to few variations. Illite is more varied. The chemical composition of smectites

is similar to pyrophyllite and talc. Montmorillonite is a principal constituent of bentonite clay deposits, which is also the main component of Fuller's earth. Kaolinite is a major component of China clay. Clay fillers are composed of a mixture of various minerals which are found in unique composition in a particular place. The name "clay" implies that particles of the material are very fine.

These fillers are discussed in separate sections, such as attapulgite, bentonite, sepiolite, kaolin, and vermiculite. Here, discussion is limited to ball clay. The name ball clay is derived from the original method of mining this plastic clay in England, where it was cut from the bank in a form of balls weighing 33 lbs. This expression was adopted to a wide range of clay materials which cannot be categorized as kaolins or fire clays.²⁵³ The majority of ball clay is used for production of china and tiles. Only some grades are manufactured for application as fillers. These grades are covered in the table above.

USA ball clays are acidic to neutral and UK ball clay is alkaline which is an important factor in filler reinforcement where acid/base interaction plays a key role.

2.1.25 COPPER²⁵⁴⁻²⁵⁸

Names: copper spheres, copper powder, bronze powder, brass powder		CAS #: 7440-50-8
Chemical formula: pure metal or metal alloy		Functionality: none
Chemical composition: copper powder: Cu - 98.5-99.5%; bronze powder: Cu - 88%, Sn - 10%; brass powder: Cu - 70-90%, Zn - 30-10%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 8.92	Mohs hardness: 2.5-3	Melting point, °C: 1083
CHEMICAL PROPERTIES		
Chemical resistance: reactive with acids, alkalis, and oxygen		
ELECTRICAL PROPERTIES		
Resistivity, Ω-cm: 1.6 x 10 ⁻⁶		
MORPHOLOGY		
Particle shape: dendritic, spherical of spheroidal (water atomized)		Aspect ratio: 1-3
Particle size, μm: 1.5-5	Sieve analysis: 325 mesh residue - 0.5%	
MANUFACTURERS & BRAND NAMES: AcuPowder, Union, NJ, USA manufacturer of a range of copper, brass, and bronze powders. Ultrafine copper powder 2000, Spherical copper powder A 155 and 500, Bronze powders 5631 and 201 have particle size suitable for thin film applications		
MAJOR PRODUCT APPLICATIONS: conductive plastics and paints		
MAJOR POLYMER APPLICATIONS: epoxy, PP, PA, PE		

Copper powder undergoes oxidation when it is contacted with air during cooling process. There are annealed grades available in which the surface oxides are reduced by hydrogen to the pure copper. There are four types of copper powder: electrolytic (irregular porous particles or dendrite shaped aggregates of smaller particles), flake (made by machining), spherical (gas atomized which consists of spherical particles), and spheroidal (water atomized having elongated particles).²⁵⁸

2.1.26 CRISTOBALITE²⁵⁹⁻²⁶⁴

Names: cristobalite		CAS #: 14464-46-1
Chemical formula: SiO ₂	Functionality: OH and from silane treatment	
Chemical composition: SiO ₂ - 99-99.7%, Al ₂ O ₃ - 0.07-0.25%, Fe ₂ O ₃ - 0.03-0.05%		
Trace elements: Ti, Ca, Na, Mg, K		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.32	Mohs hardness: 6.5	Loss on ignition, %: 0.15-0.2
Coefficient of thermal expansion, 1/K: 54x10 ⁻⁶		
CHEMICAL PROPERTIES		
Chemical resistance: chemically inert		
Moisture content, %: 0.006-0.1	pH of water suspension: 8.5	
OPTICAL PROPERTIES		
Refractive index: 1.48	Brightness: 91-95	Whiteness: 92-96
Color: Y tristimulus value: flour - 90-92, micronized - 95-96		
MORPHOLOGY		
Crystal structure: tetragonal	Oil absorption, g/100 g: 21-28	Hegman fineness: 5.5-7
Particle size, µm: 0-6 (micronized), 0-200 (coarse)		Specific surface area, m ² /g: 0.4-6.5
MANUFACTURERS & BRAND NAMES: C.E.D. Process Minerals, Akron, OH, USA Goresil KRS, C-100, C-200, C-325, C-400, 1045, 835, 525, 215, 210 - synthetic cristobalite of varying particle sizes Quarzwerke, Frechen, Germany Cristobalite flour M 002, M 006, M 0010, M 3000 - untreated synthetic cristobalite of different particle sizes Sikron cristobalite flour SF3000, SF4000, SF6000 - micronized untreated cristobalite flours of different particle sizes Silbond 006 MST, 3000 MST, 3000 RST-M, 4000 MST, 6000 EST, 6000 MST, 6000 RST, 8000 RST, 8000 TST - micronized treated cristobalite flours (EST - epoxysilane, MST - methacrylsilane, RST - trimethylsilane, TST - methyl silane)		
MAJOR PRODUCT APPLICATIONS: exterior paints, coatings, synthetic plastering compounds, thermoplastic road marking compounds, adhesives, sealants, plastics, abrasives, cables, stucco, kitchen sinks and laminates, dental, military, electronics		
MAJOR POLYMER APPLICATIONS: epoxy, polyurethane, PMMA, rubber, PVC, unsaturated polyester, silicone, acrylics		

Cristobalite is a polymorph of quartz, meaning that it is composed of the same chemistry, SiO₂, but has a different structure. Both quartz and cristobalite are polymorphs of quartz group. Cristobalite is not found in sufficient quantities in natural source. For commercial purposes, it is synthetically produced from sand by heating in kiln to 1500°C. The resultant white powder is used as a filler or it is micronized

and surface treated. The most important properties of cristobalite are its whiteness and durability on exposure to environmental conditions. Products manufactured by Quarzwerke GmbH are treated with the following silanes: epoxy, methacrylate, trimethyl, and methyl silane.²⁶¹⁻²⁶³

Several essential properties of cristobalite have influence on its applications. They include lower density than quartz (higher volume at the same mass), purity (low catalytic effect on many polymeric systems, excellent properties in exterior coatings due to low level of iron oxide), very low moisture (no need for drying in moisture sensitive systems), pure white color, less abrasive due to filler particle morphology.

2.1.27 DIATOMACEOUS EARTH²⁶⁵⁻²⁶⁶

Names: diatomaceous earth, diatomite		CAS #: 68855-54-9	
Chemical formula: SiO ₂		Functionality: OH	
Chemical composition: SiO ₂ - 85.5-91.8%, Al ₂ O ₃ - 3.2-4.5%, CaO - 0.3-0.6%, Fe ₂ O ₃ - 1-1.4%, K ₂ O - 0.-1.2%, Na ₂ O - 0.5-3.6%, TiO ₂ - 0.1-0.2%			
PHYSICAL PROPERTIES			
Density, g/cm ³ : 2-2.5		Loss on ignition, %: 0.1-5	
CHEMICAL PROPERTIES			
Chemical resistance: chemically inert		pH of water suspension: 6.5-10	
Moisture content, %: 0.2-6		Adsorbed water, %: 190-600	Water solubility, %: 0.1-1
OPTICAL PROPERTIES			
Refractive index: 1.42-1.48		Brightness: 70-90	
Color: white, off white, gray, buff, pink			
MORPHOLOGY			
Porosity: 85% (void space), pore size - 1.5-22 μm (in filter aids)			Particle size, μm: 3.7-24.6
Hegman fineness: 0-5.5		Oil absorption, g/100 g: 105-190	
Sieve analysis: 325 mesh residue - trace to 17.6%			Specific surface area, m ² /g: 0.7-180
MANUFACTURERS & BRAND NAMES: Eagle-Picher Minerals, Inc., Reno, NV, USA Celatom Natural Fine Fillers: MN-2, MN-3, MN-4, MN-5, MN-8, LCS-3 natural grades differing in particle size Celatom Flux Fine Fillers: Ultrabloc, Cela-Brite, MW-25, Ultraflat, MW-27, MW-31, MW-32 fillers designed for different applications listed below Celatom line of filtering and polishing media Grefco Minerals, Inc., Torrance, CA, USA Dicalite Natural Diatomite Functional Fillers: 104, CA-3, IG-3, 143, SA-3, 182 Dicalite Processed Diatomite Functional Fillers: WF, WFAB, 395, WB-5, L-5, L-10, SP-5, PS, SF-5 World Minerals, Inc., Celite, Lompoc, CA, USA Celite 289, 266, 110, 281, 315, 270, 292, 350, White Mist, 499, Super Fine, Super Floss, Snow Floss, HSC - fillers designed for different applications in rubber, paper, paint, polishers, cleaners, catalysts			
MAJOR PRODUCT APPLICATIONS: paints, coatings, rubber, abrasive polishes, cleaning waxes, seed coatings, anticaking agent, antiblock applications, pesticide formulations, asphalt extender, automotive windshields, catalyst support, concrete additive, dental molds, drilling mud, filter papers and pads, specialty papers, paperboard, foundry, waste disposal aids, stucco, battery boxes, plastic film			
MAJOR POLYMER APPLICATIONS: rubber, PE, alkyd, acrylics, silicone			

Diatomite is a chalky sedimentary rock composed of skeletal remains of diatomites. Diatomites are single-cell aquatic plants living in the oceans. There is a great variety of diatomites as shown in Figure 2.23. The micrographs show the complicated structure of diatomites which explains their high porosity and thus the effect they

have on gelling of liquids and on rheological properties. It is estimated that there are more 25,000 species of diatoms.

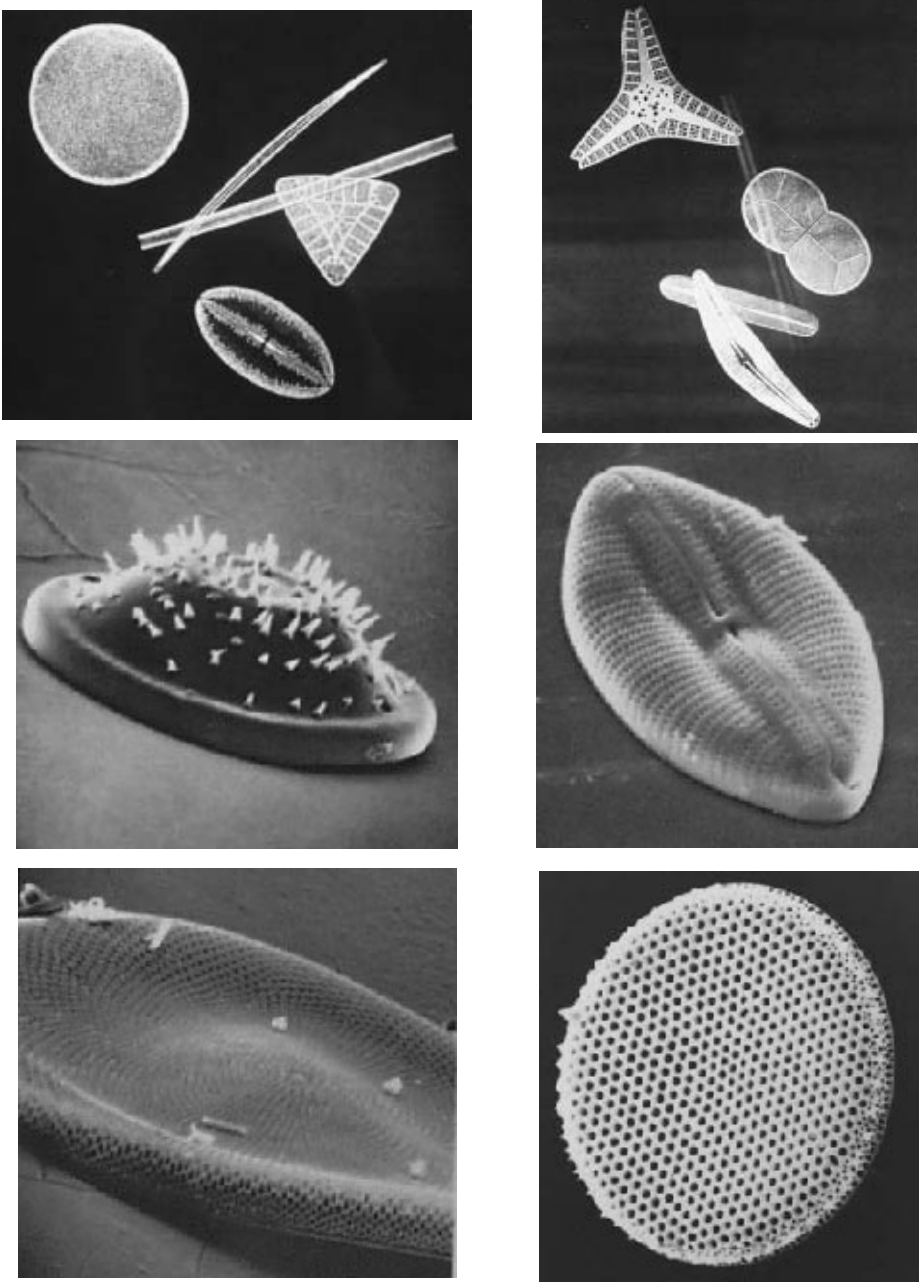


Figure 2.23. SEM micrographs of diatomites. *Courtesy of World Minerals, Inc., Lompoc, CA and Grefco Minerals, Inc., Lompoc, CA (figures in the first row).*

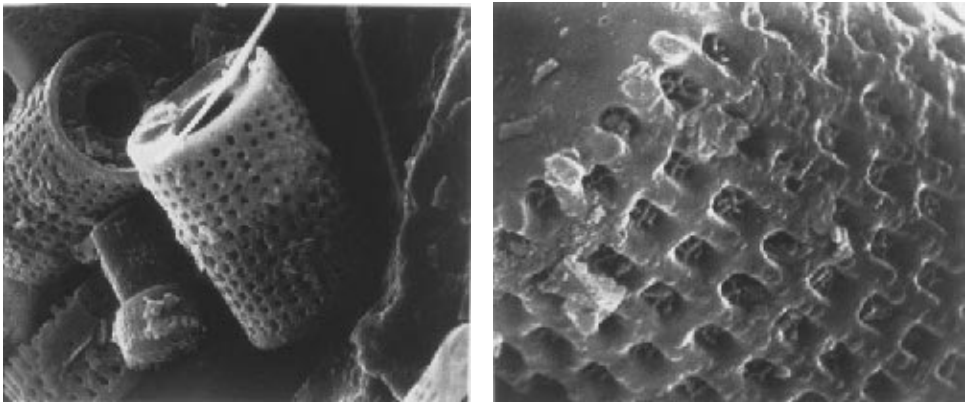


Figure 2.23 (continuation). SEM micrographs of diatomites. *Courtesy of Eagle-Picher, Reno, NV.*

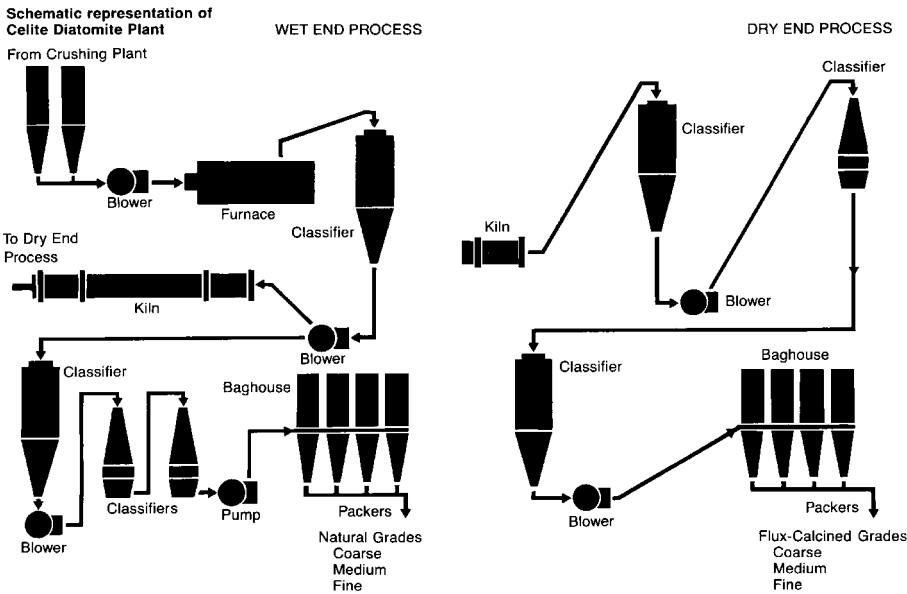


Figure 2.24. Schematic representation of the production process for diatomaceous earth fillers. *Courtesy of World Minerals, Inc., Lompoc, CA, USA.*

Figure 2.24 shows the method of processing of diatomite to different grades of fillers. The natural grades are uncalcinated powders which are crushed and classified according to particle size distribution. In this process moisture is also removed. Natural diatomite contains 40% moisture. In the production of the calcinated and the flux-calcinated products, large kilns are used. The high

temperature process causes sintering of the diatom particles to clusters in which the characteristic structures of diatomites are maintained. The process is completed by classification and packaging.²⁶⁶

Diatomaceous earth fillers play several roles, such as rheological additives (absorb liquids in pores to increase viscosity on standing and release them on mixing) and flatting agents. They are useful to increase the rate of paint drying (porous filler assists evaporation), to improve sanding properties, to increase mechanical adhesion of coatings, and to reduce the amount of TiO_2 needed to produce whiteness or opacity in a material. Due to their chemical inertness, these fillers do not interfere with the other components of the mixture. The grade selected depends on the surface smoothness required, the degree of flatting, and the type of dispersion equipment used. It is also important to choose other co-fillers. It is, for example, known that a combination of diatomaceous earth and talc provides paint with good properties.

2.1.28 DOLOMITE²⁶⁷

Names: dolomite		CAS #: 16389-88-1
Chemical formula: CaMg(CO ₃) ₂		Functionality: none (OH in admixtures)
Chemical composition: CaCO ₃ - 55%, MgCO ₃ - 43%, SiO ₂ - 0.7%, Al ₂ O ₃ - 0.2%, Fe ₂ O ₃ - 0.3%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.85	Mohs hardness: 3.5-4	
CHEMICAL PROPERTIES		
Chemical resistance: reacts with acids		Moisture content, %: 0.1
OPTICAL PROPERTIES		
Color: white, yellow, gray, or brown (if iron is present)		
MORPHOLOGY		
Crystal structure: trigonal	Cleavage: three directions forming rhombs	
MANUFACTURERS & BRAND NAMES: Charles B. Chrystal Co., Inc., New York, USA KF, DF 1000, DF 2000, DF 3000 differing in particle sizes Omya/Plüss-Staufer AG, Oftringen, Switzerland		
MAJOR PRODUCT APPLICATIONS: similar to calcium carbonate with exception of food, pharmaceutical and sugar industries		
MAJOR POLYMER APPLICATIONS: the same as in calcium carbonate		

2.1.29 FERRITES²⁶⁸⁻²⁷⁰

Names: ferrites, magnetic fillers		CAS #: various
Chemical formula: Ba/Sr carbonate with ferric oxide, NiZn, MnZn, CuZn, iron silicide, BaO·Fe ₂ O ₃ , SrO·6Fe ₂ O ₃ , (Mn,Zn) _y (Fe ₂ O ₃) _{2-zn} , BaPb, BaSrPb, Nd ₂ Fe ₁₄ B		Functionality: none
Chemical composition: variable		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.3-5.1		
CHEMICAL PROPERTIES		
Chemical resistance: some grades are rust resistant, chemically resistant		
ELECTRICAL PROPERTIES		
Dielectric constant: 8-22	Magnetic saturation, emu/g: 40-109	
Resistivity, Ω-cm: 10 ² -10 ¹⁰	Volume resistivity, Ω-cm: 10 ¹⁰	
MORPHOLOGY		
Particle size, μm: 0.05-14	Oil absorption, g/100 g: 10.8-14.8	
Aspect ratio: 1-5	Specific surface area, cm ² /g: 210-6000	
MANUFACTURERS & BRAND NAMES: Cortex Biochem, San Leandro, CA, USA A broad range of biochemical aids used for magnetic separation of biological materials. The following lines of products are manufactured: MegaCell (magnetizable cellulose/iron oxide), MagAcrolein (magnetizable polyacrolein/iron oxide), MagaChar (magnetizable charcoal), MagaBeads (magnetizable particles), MagaPhase (ion exchange products) Steward, Chattanooga, TN, USA NiZn Ferrite 72800, 72500 MnZn Ferrite 73300 CuZn Ferrite 126800 Iron silicide Fine, Corse Wright Industries, Inc., Brooklyn, NY, USA Magnetic pigments 5000, 3000, 3006, 4000, 4200, 12672, 112978, 41183		
MAJOR PRODUCT APPLICATIONS: plastic magnets, xerographic materials, filters, fibers, energy attenuating powders, microwave absorbing materials		

Cortex Biochem has found interesting applications for magnetizable particles in analytical fields. Particles of the analytic aid are prepared from a combination of magnetizable materials (iron oxide) and absorbing material (e.g., charcoal, polyacrolein, ion exchange, cellulose). The particles are dispersed in a biological sample to selectively absorb required compounds. After absorption was accomplished, particles with absorbed substance are removed from solution by a magnetized rod. The materials are used for separation of enzymes, protein, cells or bacteria.

2.1.30 FELDSPAR

Names: feldspar		CAS #: 14808-60-7
Chemical formula: (Na or K or Ca)Al ₁₋₂ Si ₃₋₂ O ₈		Functionality: OMe, OH
Chemical composition: SiO ₂ - 68.4-76.8%, Al ₂ O ₃ - 14-18.8%, Fe ₂ O ₃ - 0.005-0.06%, CaO - 1.1-1.5%, K ₂ O - 2.8-4.1%, Na ₂ O - 4.9-6.5%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.55-2.76	Mohs hardness: 6-6.5	
CHEMICAL PROPERTIES		
Moisture content, %: 0.1	pH of water suspension: 8.2-9.3	
OPTICAL PROPERTIES		
Refractive index: 1.53	Brightness: 90-94	
Color: white; L - 96-96.7, a - -0.3 to -0.4, b - 0.5-1.3		
MORPHOLOGY		
Particle shape: sub-angular	Crystal structure: monoclinic to triclinic	
Particle size, μm: 3.2-14	Oil absorption, g/100 g: 22-30	Hegman fineness: 0-7
Sieve analysis: 325 mesh sieve residue - traces		Specific surface area, m ² /g: 0.8-4
MANUFACTURER & BRAND NAME: Feldspar Corporation, Atlanta, GA, USA NC-4 - feldspar for ceramic applications Kentucky-Tennessee Clay Company, Mayfield, KY, USA Minspar 3, 4, 7, 10 with particle size decreasing as the grade number increases		
MAJOR PRODUCT APPLICATIONS: paints, coatings, plastics, rubber, adhesives, sealants		
MAJOR POLYMER APPLICATIONS: alkyd, acrylic, rubber, polyurethanes, epoxy		

The feldspar group is a fairly large group with nearly 20 members recognized, but only nine are well known and common. Those few, however, make up the greatest percentage of minerals found in the Earth's crust. The following are some of the more common feldspar minerals: *The plagioclase feldspars*: Albite - sodium aluminum silicate; Oligoclase - sodium calcium aluminum silicate; Andesine - sodium calcium aluminum silicate; Labradorite - calcium sodium aluminum silicate; Bytownite - calcium sodium aluminum silicate; Anorthite - calcium aluminum silicate; *The K-feldspars or alkali feldspars*: Microcline - potassium aluminum silicate; Sanidine - potassium sodium aluminum silicate; Orthoclase - potassium aluminum silicate.

2.1.31 GLASS BEADS²⁷¹⁻²⁹⁷

Names: glass bead, microspheres, solid beads, hollow microballoons		CAS #: 65997-17-3
Chemical formula: SiO ₂	Functionality: OH or depends silane treatment	
Chemical composition: <i>A-glass</i> : SiO ₂ - 72-73%, Na ₂ O - 13.30-14.3%, K ₂ O - 0.2-0.6%, CaO - 7.2-9.2%, MgO - 3.5-4%, Fe ₂ O ₃ - 0.08-0.2%, Al ₂ O ₃ - 0.8-2%; <i>E-glass</i> : SiO ₂ - 52.5%, Na ₂ O - 0.3%, K ₂ O - 0.2%, CaO - 22.5%, MgO - 1.2%, Fe ₂ O ₃ - 0.2%, B ₂ O ₃ - 8.6%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.46-2.54 (solid), 0.12-1.1 (hollow)	Mohs hardness: 6 (A-glass), 6.5 (E-glass)	
Softening point, °C: 704 (A-glass), 846 (E-glass)		Annealing point, °C: 548
Compressive strength, MPa: up to 70,000 MPa (solid)		Specific heat, kJ/kg · K: 1.17
Young modulus, GPa: 68.9 (E-glass)		Poisson ratio: 0.21
Coefficient of thermal expansion: 85x10 ⁻⁷ (A-glass), 28x10 ⁻⁷ (E-glass)		Coefficient of friction: 0.9-1
CHEMICAL PROPERTIES		
Chemical resistance: resistant to most chemical environments similar to glass		
Silanes used for treatment: dimethyldiethoxy silane, 3-(methacryloxy) propyltrimethoxy silane, vinyl triethoxy silane, amino silane. Silane coating was estimated to be 0.2 wt%. ^{277,292} Treatment with epoxy silane has been used ²⁷⁹ followed by PS-maleic anhydride grafting through amine spacer.		
pH of water suspension: 7-9.4		
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 1.51 (A-glass - soda lime) 1.55 (E-glass - borosilicate)		Dielectric constant: 1.2-7.6
Color: white or transparent (solid beads)		Dielectric strength, V/cm: 4500
Resistivity, Ω-cm: 10 ⁷	Volume resistivity, Ω-cm: 10 ¹² -10 ¹⁶	
MORPHOLOGY		
Particle size, μm: 7-8	Oil absorption, g/100 g: 17-20	Wall thickness, μm: 1-20
Sieve analysis: 325 mesh residue - traces to 15%		
DBP absorption, cm ³ /100 g:	Specific surface area, m ² /g: 0.4-0.8	
MANUFACTURERS & BRAND NAMES:		
3M Specialty Additives, St. Paul, MN, USA Scotchlite Glass Bubbles, General Purpose Series K1, K15, K20, K25, K37, K46, S22, S32, S38, B38, S60 hollow glass bubbles manufactured from soda-lime borosilicate glass (low density beads varying in density in a range from 0.12 to 0.6 g/cm ³ which gives a crush strength of 1.7-69 MPa or 250-10,000 psi)		
Abrasivos y Maquinara, SA, Barcelona, Spain Microcel M borosilicate glass spheres in a density range from 0.18 to 0.35 g/cm ³ which have a crushing strength of 6-15 MPa or 900-2200 psi		
Duke Scientific, Palo Alto, CA USA Spherical glass material, solid and hollow glass microspheres in ranges of particle size 1-515 μm to be used as standards in scientific studies on sedimentation, separation, insulation, reflection and as spacer pigments		
continued on the next page		

MANUFACTURERS & BRAND NAMES:	
Grefco Minerals, Inc. Torrance, CA, USA	Dicaperl HP-110, HP-210, HP-510, HP-710, HP-910 two series of these hollow glass bubbles are produced: standard - 10 series and high performance - 20 series which has one of the two proprietary coatings used to increase adhesion (the density is in the range of 0.18-0.25 g/cm ³ which indicates that these are light weight bubbles)
JB Company, Franklin, NJ, USA	a specialty products manufacturer produces a variety of solid glass beads, clear and colored, used for decorative purposes in industrial products
MO-SCI Corporation, Rolla, MO, USA	produces a range of specialty products such as Indentisphere (glass microspheres which can be identified by their fluorescent, magnetic or radioactive properties, e.g. identification of explosives); Duraspheres (borosilicate glass spheres for pharmaceutical applications and electronics); Bioactive Glass (restorative purposes in medical and dental applications)
Potter Industries, Inc., Valley Forge, PA, USA	Spherglass, A-glass 1922, 2024, 2227, 2429, 2530, 2900, 3000, 4000, 5000, 6000 (the higher the number, the smaller particle size in the range of 7-203 μm) Spherglass, E-glass 3000E, 4000E, 5000E, 6000E (the higher the number, the smaller particle size in the range of 7-35 μm) Potter Industries developed the following surface coatings: CP-01, CP-02, CP-03, CP-26. Glass spheres are offered with a coating for the polymer to which the spheres are to be added. Spherglass beads have densities up to 1.08 g/cm ³ and they can withstand pressure of 207 MPa (30,000 psi) Spherichel 110P8 - hollow borosilicate glass spheres developed for paints and thermoplastic molding applications
Sovitec France SA, Florange, France	Micropearl 50, 90, 50100, 1020 - soda-lime glass, solid glass microspheres of different grain sizes in the range of 20-212 μm. Company manufactures the above grades with three surface finishes 215, 216, 217 which are different coupling agents selected for different types of thermoplastic and thermosetting resins. Numerous applications in plastic industry are documented by the results characterizing performance.
The PQ Corporation, Valley Forge, PA, USA	Q-Cel hollow spheres 300, 2116, 2106, 692OL, 636D, 640D, 6717, 7019, 5043 beads differ in density and particle size with the general trend being that larger beads are lighter (low density beads in the density range 0.19-0.48 g/cm ³ and working pressures in the range 1.7-21 MPa or 250-3000 psi)
MAJOR PRODUCT APPLICATIONS: bowling balls, cast polyester, foam, caulk, explosives, putties, sealants, pipe insulation, potting compounds, speckling compounds, reflective paints, golf balls, pultrusion, aerospace, marine, automotive, composites, and many more	
MAJOR POLYMER APPLICATIONS: PVC, polyester, polyurethane, epoxy, acrylics, POM, ABS, PA, PC, PE, PI, PMMA, PPO, PP, PS, PSF, melamine, phenoxy, silicone	

The processing technology determines the selection of the glass bubbles. To minimize the breakage of bubbles they should be added at the end of the process. Low shear and high flow mixers are required to obtain full benefits. The following mixers are suitable: double planetary, planetary, propeller, flat blade, sigma. The following mixers should not be used for thin wall bubbles: high speed disperser, colloid mill, three roll mill, homogenizers, and impingement mixers. The pumping of materials containing glass bubbles must be carefully controlled. The hydrostatic pressure generated by the pump should be lower than the maximum hydrostatic pressure which glass bubbles can withstand. The clearance between intermeshing gears in gear pumps must be greater than the bubble diameter. The following

pumps are suggested by 3M: double diaphragm, piston, progressive cavity and rotary pumps. Similar consideration of pressure should be given to the conditions of extrusion and injection molding. The crush strength of hollow beads manufactured by Potter Industries exceeds 200 MPa (30,000 psi) which is considered sufficient to survive injection molding and high shear mixing equipment. Further discussion of the relationship between crushing strength and density can be found below.

According to Potters Industries, A-glass is suggested for the majority of polymers with the exception of acetal and PTFE where E-glass should be used. The reason for surface modification of glass beads is explicitly illustrated in Figure 2.25. Coated spheres adhere to the matrix but uncoated spheres are easily delaminated from the matrix. Adhesion depends on the selection of coating for a particular matrix polymer.

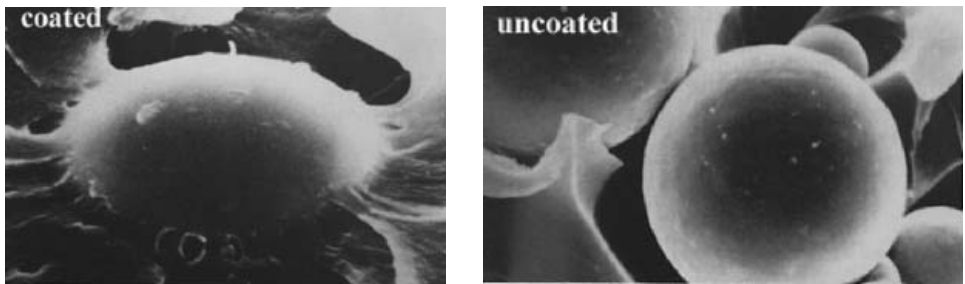


Figure 2.25. Coated and uncoated spheres in polymer matrix. *Courtesy of Potters Industries, Inc., Valley Forge, PA, USA.*

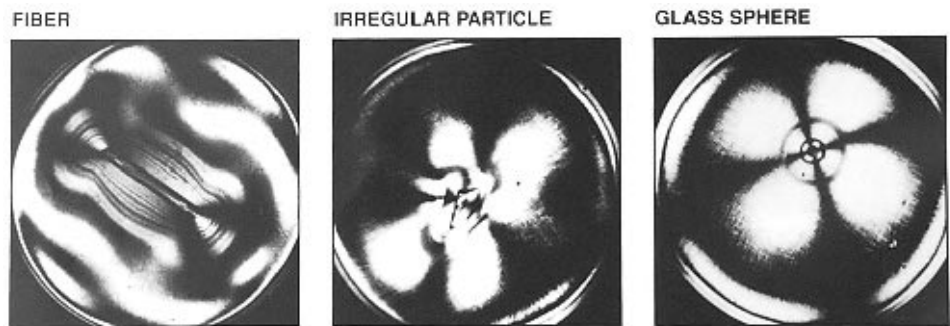


Figure 2.26. Stress distribution around fiber, irregular particle, and glass sphere. *Courtesy of Potters Industries, Inc., Valley Forge, PA, USA.*

Figure 2.26 shows one of the reasons why spherical fillers give good performance in compounded materials. The birefringence patterns show stress distribution in the vicinity of various shapes of inclusions – only with a spherical shape and a good adhesion to the matrix, uniform stress distribution is observed. Stress distribution is an essential element of material design.

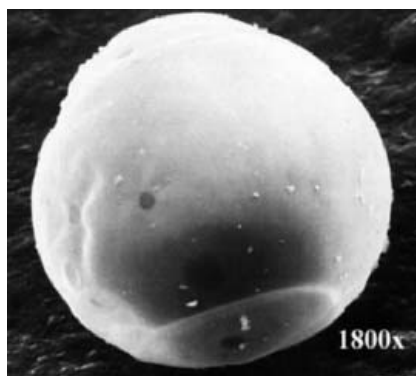


Figure 2.27. Dicaperl HP-510. Magnification 1800x. Courtesy of Grefco Minerals, Inc., Torrance, CA, USA.

Glass beads improve or control several properties of materials. These include density reduction, flow properties, viscosity decrease, rheological properties including thickening and non-sag properties, nailing, sanding, shrinkage reduction, impact strength, stiffness, tensile strength, flexural strength, and hardness, explosives performance, and acoustical properties.

The most useful feature of glass beads is their ability to reduce the density of a product. There is a trade off between the mechanical properties of beads and their density. If beads

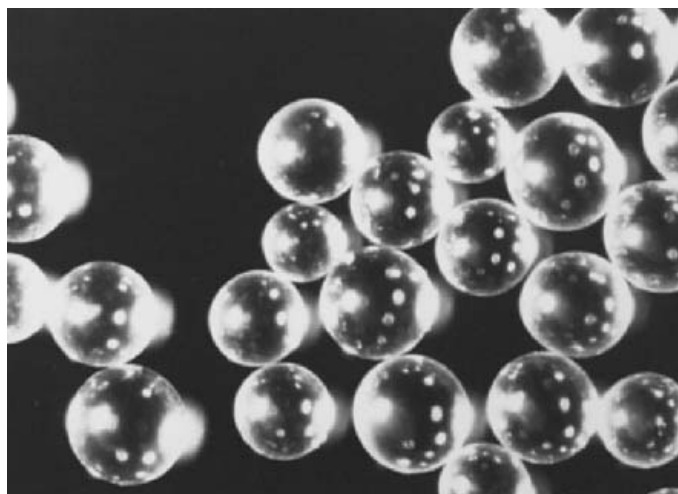


Figure 2.28. Micropearl solid glass beads. Courtesy of Sovitec France SA, Florange, France.

are very light they are also very fragile because their walls are very thin and the types of products and manufacturing methods are limited. But if they can be successfully incorporated they result in a substantial reduction in product density. If the beads are mechanically resistant they have thicker walls and do not reduce density of neat polymers. The density of hollow spheres available in the market varies from 0.12 to 1.1 g/cm³. This means that glass occupies from about 10 to 50% volume of the bead which results in considerable differences in their mechanical performance. The data on the densities and crash strength for individual brands are given in table of manufacturers and brand names.

Figure 2.27 shows the morphology of a single hollow glass sphere which has a regular spherical shape. Figure 2.28 shows the morphology of solid glass beads.

2.1.32 GOLD²⁹⁸⁻³⁰⁰

Names: gold powder, gold flakes, gold spheres		CAS #: 7400-57-5
Chemical formula: Au	Functionality: none (possible thiol derivatization) ³⁰⁰	
Chemical composition: Au - 99.96%		
Trace elements: Cu, Fe, Pd, Ag		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 18.8	Mohs hardness: 2.5 - 3	Melting point, °C: 1064
MORPHOLOGY		
Particle size, μm: 0.8-9	Crystal structure: isometric	Cleavage: absent
Specific surface area, m ² /g: 0.05-0.8		
MANUFACTURER & BRAND NAMES: Shoei Chemical, Inc., Japan Technic, Inc., Woonsocket, RI, USA Gold Powder 507, 508, 509, 510 - chemically precipitated, spherical powder for thick conductive inks Gold Flake/Sphere 550 (thick), 555 (thin flake) - chemically precipitated flakes for conductive inks Gold Flake 552, 554, 560 precipitated/mechanically worked flakes for conductive inks and adhesives		
MAJOR PRODUCT APPLICATIONS: conductive inks, coatings, and adhesives		

Figure 2.29 shows morphology of gold powder and gold flakes.

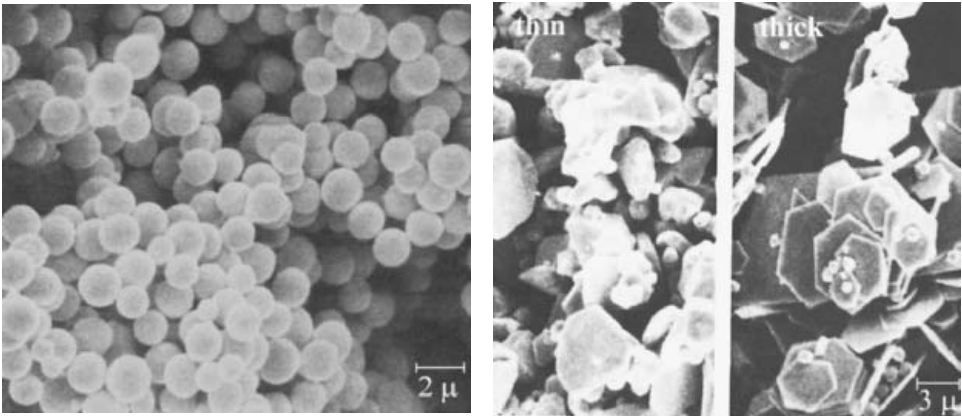


Figure 2.29. Gold powder (magnification 5250x) and thin (550) and thick (555) flakes (magnification 3200x).
Courtesy of Technic, Inc., Woonsocket, RI, USA.

2.1.33 GRAPHITE³⁰¹⁻³⁰⁹

Names: graphite, natural graphite		CAS #: 7782-42-5
Chemical formula: C		Functionality: OH
Chemical composition: carbon 80-99.97%		
Ash content, %: SiO ₂ - 48.8, Al ₂ O ₃ - 20.8, Fe ₂ O ₃ - 22.2, MgO - 2.3, CaO - 1.8, Na ₂ O - 0.4, K ₂ O - 2.2, TiO ₂ - 0.5		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2-2.25	Mohs hardness: 1 - 2	Coefficient of friction: 0.1-0.6
Thermal conductivity, W/K · m: 110-190		
CHEMICAL PROPERTIES		
Moisture content, %: 0.1-0.5		Ash content, %: 0.03-20
OPTICAL & ELECTRICAL PROPERTIES		
Color: gray	Resistivity, mΩ-cm: 0.8-2.5	
MORPHOLOGY		
Particle size, μm: 6-96	Crystal structure: hexagonal	Oil absorption, g/100 g: 75-175
Crystallite height, nm: 60-100		Cleavage: perfect in one direction
Specific surface area, m ² /g: 6.5-20	Interlayer distance, nm: 0.3354-0.336	
MANUFACTURERS & BRAND NAMES: AML Industries, Inc., Warren, OH, USA Natural Graphite Powder - Amlube 611 High Purity Graphite Powder - Amlube 610, 613 Applied Carbon Technology, Somerville, NJ, USA Three types of graphite are manufactured: natural graphite (grades A to H differing in purity and particle size), synthetic graphite (very pure L101 and high ash J101), and amorphous graphite (P100 & P103) Superior Graphite Co., Chicago, IL, USA Several lines of graphite products: amorphous graphite, crystalline flake graphite, crystalline vein graphite, Desulcu, synthetic graphite, ThermoPure. The particle sizes of these graphites are from μm to mm. Timcal Ltd., Sins, Switzerland Timrex KS 6, KS 10, KS 15, KS 25, KS 44, KS 75 graphites of irregular spheroid particle shape used in plastic materials Timrex T 44, T 75, T150 angular, flake microporous graphite Timrex SG 6, SFG 15, SFG 44, SFG 75 strong anisometric flakes, needles		
MAJOR PRODUCT APPLICATIONS: extruded profiles, batteries, conductive coatings, brake linings and clutch facings, catalysts, lubricants, self-lubricating parts, pump elements, drive shafts, thrust rings		
MAJOR POLYMER APPLICATIONS: PA-6, PA-66, PP, PS, LDPE, EPR		

Graphite is used in products for the following reasons: conductivity, EMI shielding, lubricating coatings, self-lubricating bearings, lubricants, heat, chemical, and water resistance, flame retardancy, release properties, pigmentation.

Purity, crystalline structure, texture, and particle size are factors which control tribological, thermal, electrical, chemical, and physical properties of products manufactured with graphite.³⁰⁹⁻³¹⁰ Purity can be assessed based on ash content, moisture, and trace elements. For lubricating materials, silicon carbide-free graphite is demanded, because silicon carbide is a highly abrasive material. Such grades are produced by synthetic methods. Superior Graphite Co. patented a high temperature furnace technology which can make graphite having 99.97% carbon. Also Timcal offers grades of similar purity. The following analysis of the effect of graphite is made based on the data from a broad application studies conducted by Timcal.³⁰⁹⁻³¹⁰

Self-lubricating properties were assessed based on studies of polyamide-6 and polystyrene. The friction coefficient was reduced by 30% with the addition of 30% graphite with only a small increase in wear. The friction coefficient of plastic filled with graphite depends on the purity and the crystallinity of graphite but it also depends on the concentration of graphite. In polystyrene both friction coefficient and the wear decreased as the graphite content was increased up to the peak level of 30%. Further increase in graphite concentration contributed to the increase in both wear and the coefficient of friction. Similar observations for PTFE/graphite system were explained by an increase in the porosity of the composite when it contains more than 30 wt% graphite. It is the porosity that is responsible for an increased wear rate.³⁰⁴ Glass fiber reinforced SMC and BMC compounds are particularly abrasive. The ratio of graphite to fibers and the overall content must be optimized to achieve a reduction in both wear and friction coefficient.

The mechanical properties of graphite filled plastic can be tailored to meet requirements. The studies on PA-6 show that an addition of graphite increases hardness only slightly (10%). But, the hardness of LDPE can be increased by 25%. If hardness must be increased, a smaller particle size graphite should be selected. The Young's modulus of LDPE can be tripled by the addition of up to 30% graphite. A similar addition to polyamide-6 doubled its Young's modulus. Again smaller particle size graphite is more effective.

Graphite had little influence on the tensile properties of most, but not all grades of LDPE gave the same results. The tensile strength of PA-6 is reduced by the addition of graphite but small particle sized grades have less effect on tensile strength. Elongation of LDPE, similar to other polymers, is reduced as graphite concentration increases but there is more drastic decrease in the case of PA-6 and PA-66. The impact strength of PA-6 and PA-66 is rapidly reduced by an addition of 20-30 wt% graphite. In the case of polypropylene, not only Young's modulus increased by up to 60% by an addition of 30-35 wt% graphite but also its tensile strength was improved. Fine graphite grades improve these properties more rapidly. Impact strength and elongation of PP are decreased in a manner similar to PA. PS is another example of a polymer whose tensile strength is increased by the addition of graphite (~25%) and its Young's modulus is tripled. The elongation of

PS is not significantly reduced but only because PS has very low elongation. Unlike other polymers, the hardness of PS is reduced by the addition of graphite but its impact strength follows the same pattern of being rapidly reduced as the concentration of graphite increases.

The processability of polymers can be improved by addition of graphite. The melt flow index of PS containing graphite gradually decreases as graphite concentration increases even up to 50 wt% graphite. PP gives the same relationship with finer grades decreasing melt flow index more rapidly than the coarse ones. A similar, but less pronounced, effect is observed in LDPE.

The viscosity increase depends on particle size. Smaller particles increase the viscosity of the dispersion more rapidly but there is a big difference between the effect of graphite and carbon black on viscosity. It requires three times as much graphite as carbon black for a similar increase in viscosity.

Antistatic and conductive compounds can be manufactured with graphite. Electrical properties are also very stable. This was determined in a 2 year study during which time the volume resistivity of the graphite containing compound did not change. It is important in formulating these products to consider the effect of other fillers which may be present in the formulation. It was found that the surface resistivity of graphite filled compounds containing large particle sized calcium carbonate or aluminum hydroxide was reduced. The graphite particles should always be kept as small as possible. EPR can be formulated with a high concentration of graphite without losing its flexibility, therefore it is possible to produce flexible electrodes with a surface resistivity of only 1 Ohm.

Graphite helps to improve thermal conductivity and it also helps to process materials faster. Thermal conductivity is improved to a greater extent by graphite of small particle size and high crystallinity.

The addition of graphite to polymeric systems increases their rate of crystallization due to an increased nucleation rate. This increases the molding and extrusion throughput.

Figure 2.30 shows the morphology of graphite which is built up from thin layers of irregularly shaped material.

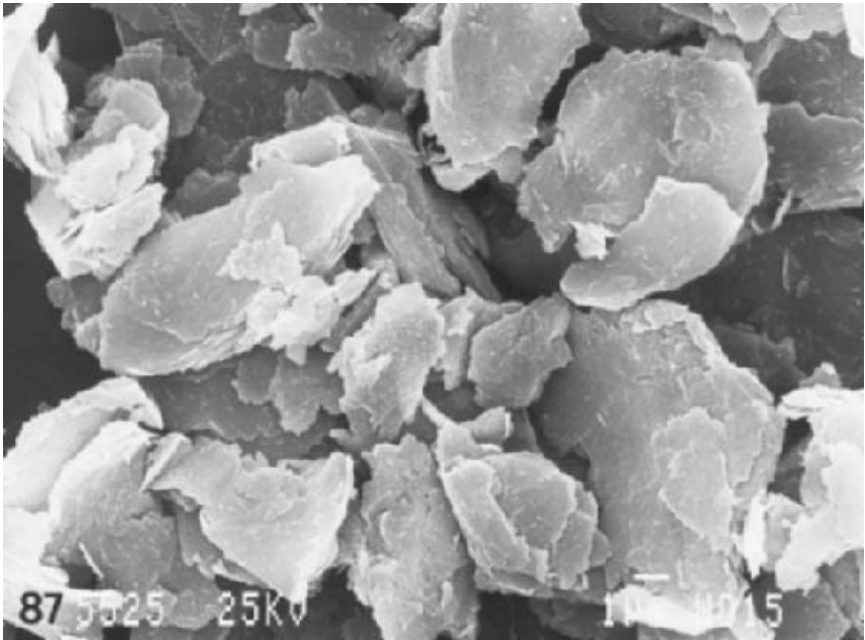


Figure 2.30. SEM micrograph of Timrex KS 15. *Courtesy of Timcal Ltd., Sins, Switzerland.*

2.1.34 HYDROUS CALCIUM SILICATE

Name: hydrous calcium silicate		CAS #: 14567-73-8
Chemical formula: SiO ₂ ·CaO·H ₂ O	Functionality: OH	
Chemical composition: SiO ₂ - 47-49%, CaO - 31-32%, Al ₂ O ₃ - 2.3-2.5%, Fe ₂ O ₃ - 0.7-0.8%, MgO - 0.6-0.7%, Na ₂ O+K ₂ O - 1.2-1.3%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.6	Loss on ignition, %: 14.9-15	
CHEMICAL PROPERTIES		
Moisture content, %: 5.5-5.8	Adsorbed moisture, %: 220-550	pH of water suspension: 8.4-9
OPTICAL PROPERTIES		
Refractive index: 1.55	Color: gray, white, off-white	Brightness: 55-90
MORPHOLOGY		
Particle size, μm: 9	Oil absorption, g/100 g: 290	Hegman fineness: 2
Sieve analysis: 325 mesh residue 2-8		Specific surface area, m ² /g: 95-180
MANUFACTURER & BRAND NAMES: World Minerals, Inc., Lompoc, CA, USA Micro-Cel A, C, E, T-21, T-26, T-38, T-49, Celkate, Silasorb synthetic fillers obtained from diatomaceous earth and lime in the process discussed below		
MAJOR PRODUCT APPLICATIONS: absorbents, carriers, flattening agents, TiO ₂ extenders, decolorizers		

Hydrous calcium silicate is produced by hydrothermal reaction of diatomaceous earth, hydrated lime, and water. Figure 2.31 gives schematic representation of the process. The product is a material which can absorb 5.5 times of its weight of water.

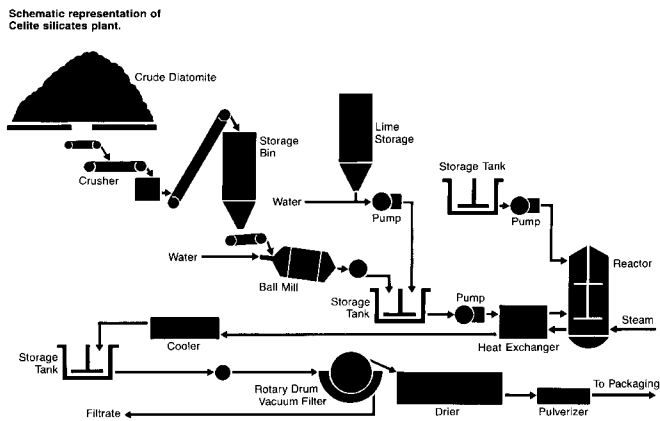


Figure 2.31. Schematic diagram of production of Micro-Cel. *Courtesy of World Minerals, Inc. Lompoc, CA, USA.*

2.1.35 IRON OXIDE³¹⁰⁻³¹⁴

Names: iron oxide		CAS #: 1332-37-2
Chemical formula: Fe ₂ O ₃	Functionality: none	
Chemical composition: Fe ₂ O ₃ - 80-99.5%, SiO ₂ - 0.03-8%, CaCO ₃ - 0-5%, Al ₂ O ₃ - 0-2%, MgO - 0-2%		
Trace elements: Pb, Ni, Cr, Sn		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 4.5-5.8	Mohs hardness: 3.8-5.1	Loss on ignition, %: 3-5
CHEMICAL PROPERTIES		
Moisture content, %: 0.1-3	pH of water suspension: 7-9	
OPTICAL PROPERTIES		
Refractive index: 2.94-3.22	Color: red, purple, gray, brown (nanosize)	
MORPHOLOGY		
Particle size, μm: 0.8-10 (26 nm - nanoparticles)	Specific surface area, m ² /g: 30-60 (nanosize)	
Sieve analysis: 325 mesh residue from traces to 10%		Oil absorption, g/100 g: 10-35
MANUFACTURERS & BRAND NAMES: Charles B. Chrystal, New York, NY, USA #3 Iron Oxide - coloring pigment for paints and flooring High Purity Iron Oxide - 99% active component, small particle size easy to disperse Miox AS - micaceous iron oxide for primers and coatings Grade W - high purity iron oxide (99% active component) for cement coloring Crocus Martis - polishing grade Nanophase Technologies Corporation, Burr Ridge, IL, USA NanoTec Iron Oxide - nanosize grade		
MAJOR PRODUCT APPLICATIONS: pigment in many materials, coatings, paints, plastics, nanocomposites		
MAJOR POLYMER APPLICATIONS: alkyd, acrylic, polyurethane, epoxy, PP		

Iron oxide is a particular example of the wide range of materials which can be obtained from grinding the natural product or synthesis. Figure 2.32 shows the morphology of nanoparticle iron oxide.

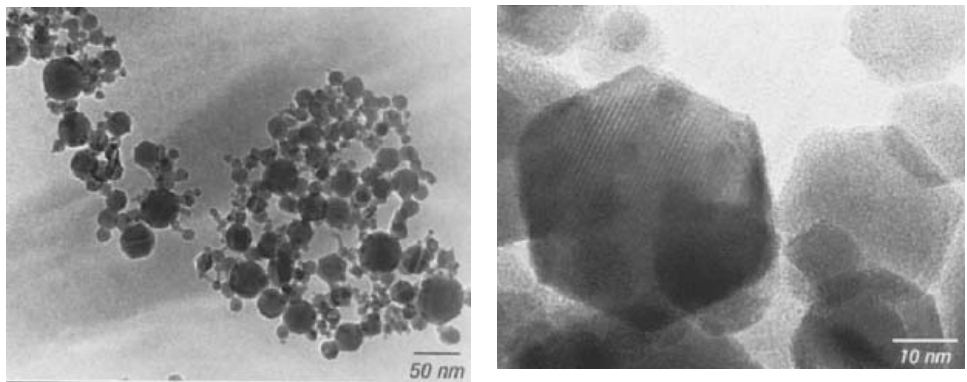


Figure 2.32. TEM micrographs of NanoTec iron oxide. *Courtesy of Nanophase Technologies Corporation, Burr Ridge, IL, USA.*

2.1.36 KAOLIN³¹⁵⁻³³¹

Names: kaolin - classified, beneficiated, calcinated, aluminum silicate, calcinated silicate, china clay, soft kaolin, hydrated aluminum silicate, kaolinite		CAS #: 66402-68-4
Chemical formula: Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O		Functionality: OH, silane modification
Chemical composition: SiO ₂ - 38.5-63%, Al ₂ O ₃ - 23-44.5%, Fe ₂ O ₃ - 0.2-1%, TiO ₂ - 0.2-1.9%, K ₂ O - 0.8-1%		
Trace elements: Pb, As		
PHYSICAL PROPERTIES		
Density, g/cm³: 2.58-2.62, 2.5-2.63 (calcinated)		
Mohs hardness: 2, calcinated 4-8		Melting point, °C: 1800
Loss on ignition, %: 12.1-14.2, 0.23 (calcinated)		Specific heat, kJ/kg · K: 4
CHEMICAL PROPERTIES		
Moisture content, %: 1-2 (up to 7%), slurry 20-30%		pH of water suspension: 3.5-11
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 1.56-1.62 (calcinated 1.62)		Whiteness: 88-91
Color: white, cream; L* - 95.04-95.70, a* - 0.11-0.30, b* - 5.25-6.4		Dielectric constant: 1.3-2.6
Brightness: 69-90 (classified), 85-91 (beneficiated), 84-95 (calcinated)		
MORPHOLOGY		
Particle shape: platy		Crystal structure: hexagonal
		Particle size, µm: 0.2-7.3
Oil absorption, g/100 g: 27-48 (classified), 50-60 (beneficiated), 45-120 (calcinated)		
Sieve analysis: 325 mesh residue - 0.01-2		Specific surface area, m²/g: 8-65
Hegman fineness: 3-7		
MANUFACTURERS & BRAND NAMES: Albion Kaolin Co., Hephzibazh, GA, USA Albion AP-750 H, AP-750 L, AP-750 M, H-007, S-60, S-75 - adhesives, caulks, sealants, soft rubber products Alcoat Plus Slurry, Plus-L Slurry - latex based slurry in high brightness applications Britefil 80 Pulverized and Slurry - paper and water-based paints Royale Slurry - kaoline dispersed with sodium polyacrylate Burgess Pigment, Sandersville, GA, USA Fine Particle Size #10, #17, #20, #40, #60, Polyclay, Thermo Glace H - hydrous aluminum silicate Ultrafine Particle Size #27, #28, #97, #98 - hydrous aluminum silicate. #27 and #28 are spray dried versions for use in water-based systems only Air Floated - #80, #86, HC-77 - hydrous aluminum silicate Calcinated grades - Icecap K, Iceberg, #30 Thermo-optic grades - Optiwhite, Optiwhite MX, Optiwhite P, 30 P (see process discussion below) Burgess 2212, 2227 - calcinated kaolin surface treated with amino silane		

continued on the next page

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MANUFACTURERS & BRAND NAMES:

Charles B. Chrystal Co, Inc., New York, NY, USA

China Clay Lion - soft kaolin for use in cosmetics, pharmaceuticals, rubber, paint, paper

Calcinated Kaolin Clay - high brightness

Plus White Kaolin - paper industry grade

Electros Kaolin USP - pharmaceutical and cosmetics grade

Kaolin SIM 90 - exceptional brightness without bleaching

D.J. Enterprises, Inc., Cleveland, OH, USA

Sillum 200 QP

ECC International, St. Austell, UK

Supreme, Speswhite, Stockalite, Devolite, Grade B, D, E, Polwhite, GTY - kaolin grades differing in particle size

PoleStar 200R, 400A, 501 - calcinated kaolins

Polarite 102A, 103A, 503A - calcinated kaolins, silane coated

Infilm Clay Range - produced to individual customer requirements

Engelhard Corporation, Iselin, NJ, USA

ASP 072, 101, 102, 170, 200, 400P, 600, 602, 672, NC, Buca, Catalpo - hydrous aluminum silicate, spray-dried or highly pulverized powders. ASP 101 is stearate coated and ASP NC is delaminated

Santitone 5, 5HB, Special, SP-33, Whitetex - calcinated kaolins

Translink 37, 77, 445, 555, HF-900 - calcinated and surface modified: vinyl functionality - 37, 77, amino functionality - remaining grades

Evans Clay Company, McIntyre, GA, USA

Snofil, Snofil Plus, Hi White - clays for paper industry of different particles sizes

Snobrite, Snobrite Special, Snobrite PG, Apex, Kaolloid, Hi White R - adhesive, caulk, paint, roofing, rubber grades

Snobrite slurry - paper, adhesive, paint roofing

J.M. Huber Corporation, Macon, GA, USA

Polyplate P, P01, 90, HTM - delaminated water washed kaolin grades for water-based coatings.

P, 90 and HTM grades are spray dried

Polygloss 90 - water washed kaolin with ultrafine particles and high brightness

Huber 35, 35B, 80, 80B, 90, 90B, HG90 - water washed kaolins for water-based systems (all grades) and solvent-based systems (all but with symbol B which means that it disperses only in water).

HG means that kaolin was spray-dried.

Huber 683, 40C, 70C, 90C - structured pigment (683) and calcinated grades (letter C) for water-based and solvent paints and coatings

Kentucky-Tennessee Clay Company, Mayfield, KY, USA

Suprex, Alumex, Supreme, Rogers - kaolins from two different locations in SC and GA

R.T. Vanderbilt Company, Inc., Norwalk, CT, USA

Bilt-Plates 145, 156 - primers and paints and unbleached kraft liner board

Continental Clay - carrier for agricultural chemicals

Dixie Clay - coatings, primers, crack fillers, caulk

Langford Clay - low cost reinforcing filler for elastomers

McNamee Clay - low cost reinforcing filler for elastomers

Par Clay, Par RG Clay - reinforcing and inert filler for elastomers

Peerless Clay #2 - crack fillers, traffic and barn paint, floor covering, primer, caulk

Sachtleben Chemie, Duisburg, Germany

Sachtosil CF, PV - controlled process results in synthetic-like material used as antiblocking additive in films

MAJOR PRODUCT APPLICATIONS: cosmetics, pharmaceuticals, rubber, tire, paint, coatings, paper, agriculture, floor covering, crack fillers, primers, films, wire and cable, electrical accessories, can sealants, roofing membranes, syringes, coated fabrics, tennis balls, urethane sealants, foam, gaskets, footwear

MAJOR POLYMER APPLICATIONS: alkyd, cellulose, rubber, polyurethanes, PVC, PE, EPDM, EPR, PA, PP

Kaolin is a product of the decomposition of granite and white feldspar. The typical feature of kaolin is extreme fineness. Over the last two centuries, China clay be-

come so popular that it is now the largest export item from the United Kingdom after North Sea oil.

Production of China clay begins with large scale mining. The mined mineral is one part China clay, 3 parts rock, 4 parts sand and one part mica. The other components are separated and either utilized or discarded. After removing of rock material, the remainder is mixed with water and passed through a hydrocyclone to remove fine sand and coarse mica. The further refining process includes thickening of materials obtained from the hydrocyclones through flocculation of particles and their subsequent separation from water in large overflow tanks. In the next stage, fine mica is removed either in hydroseparators or hydrocyclones. To further improve the quality of clay, magnetic separation is applied which removes such minerals as mica, iron oxide, and tourmaline.

From this point the clay becomes suitable for some applications but for others, it must be still refined. Clay classification is one of these stages of refining. For example, paper grades must be very fine and here a centrifugal classifier is usually used to separate finer particles. Some grades are bleached to increase their whiteness. Bleaching can be done by ozone gas or sodium hydrosulfite. Other grades are subjected to grinding. Figure 2.33 shows stacks of china clay before grinding. The grinding process reduces the size and delaminates the stacks resulting in a finer product.

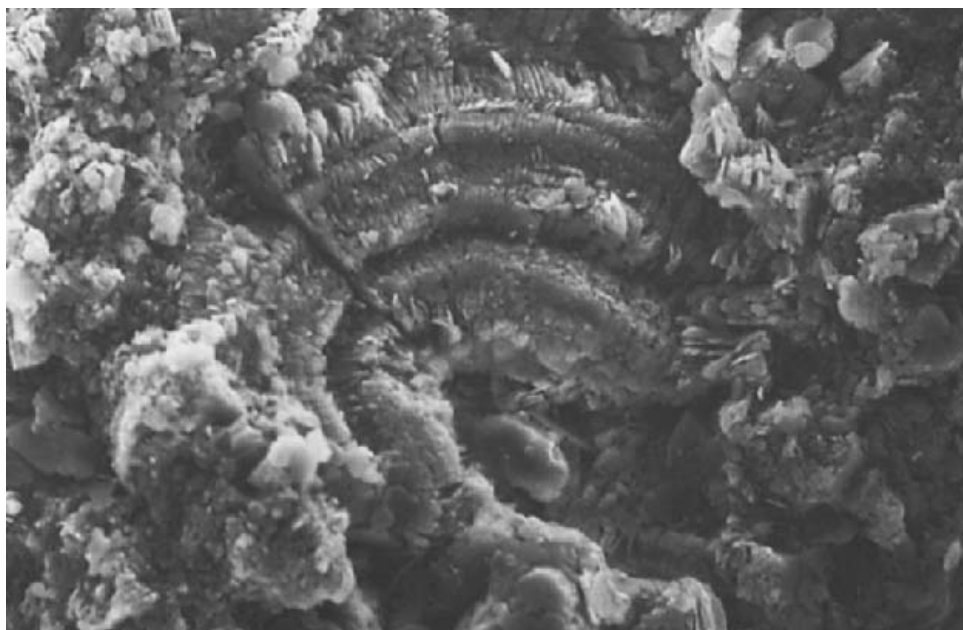


Figure 2.33. SEM micrograph of china clay before processing. *Courtesy of ECC International St. Austell, UK.*

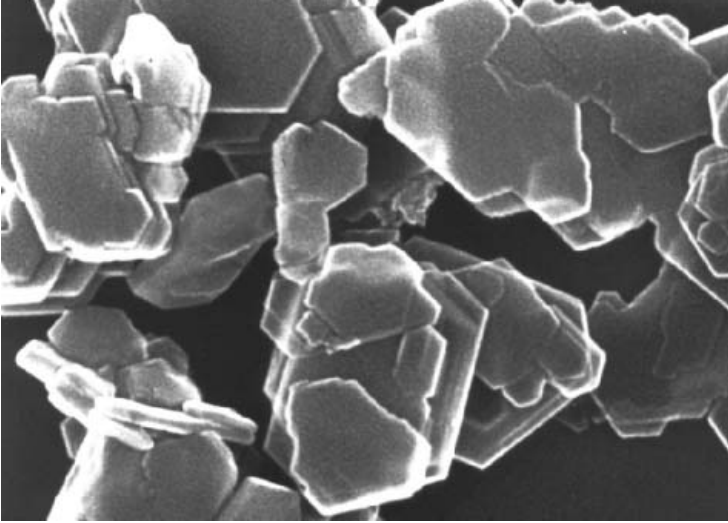


Figure 2.34. SEM micrograph of kaolin. *Courtesy of ECC International St. Austell, UK.*

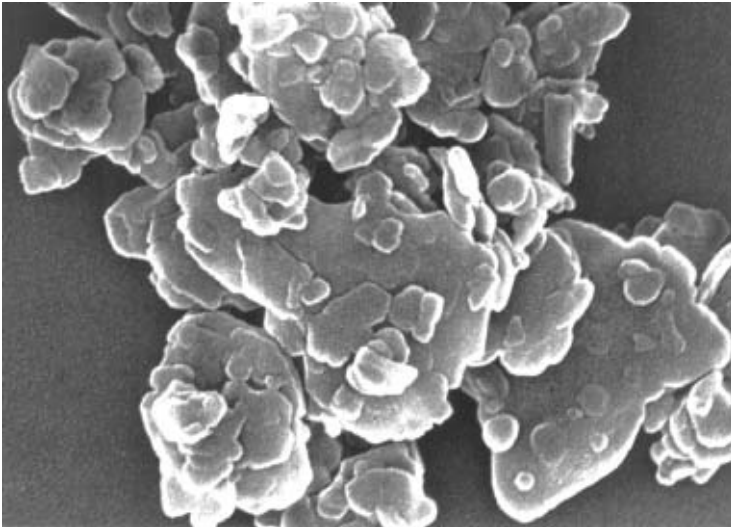


Figure 2.35. SEM micrograph of calcinated kaolin. *Courtesy of ECC International St. Austell, UK.*

Some product is sold in slurry which is a convenient form since it eliminates dust, saves energy, and lowers the cost. The industries which are frequent users of such product are paper and paints. Many other applications require material to be in a powder form, therefore the slurry is flocculated, concentrated (filter presses), and dried. Several dryer types are used such as rotary, tray, fluidized bed process or spray. The clay may be pulverized after some of these drying process depending requirements. Figure 2.34 shows the morphology of kaolin. A typical platy structure is clearly displayed on this photograph.

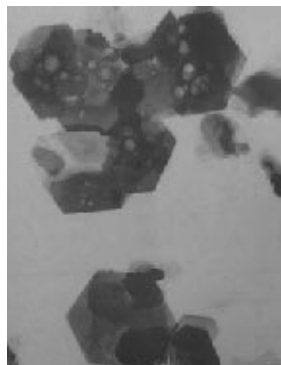


Figure 2.36. SEM micrograph of Optiwhite, thermo-optic grade. *Courtesy of Burgess Pigment, Sandersville, GA, USA.*

The process of calcination considerably changes the original properties of the material (see table above). Heating of kaolin above 450°C alters the clay structure and improves electrical resistance and brightness. The process of calcination is conducted in kilns at temperatures between 850 and 1500°C. Figure 2.35 shows calcinated kaolin which differs from dried kaolin by having round edges which is a result of the high temperature treatment.

Burgess Pigment have developed yet another method of kaolin treatment called flash calcination process. The process is conducted by a whirling upward rising stream of hot gas in the form of vortex in which material is dehydrated in a matter of seconds forming the unique morphological structure and a given the grade name “thermo-optic” (Figure 2.36). This material has lower specific gravity and very good hiding power.

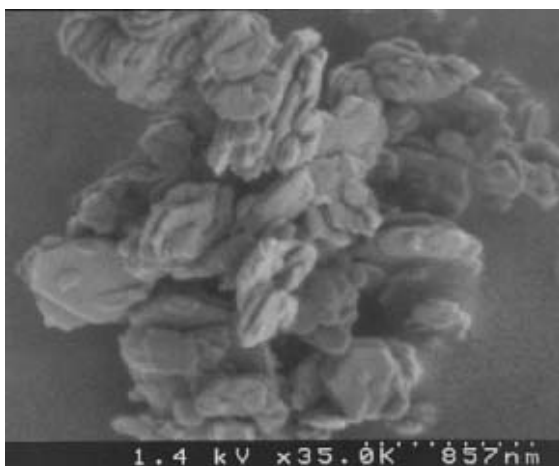


Figure 2.37. SEM micrograph of Huber – structured pigment. *Courtesy of J.M. Huber Corporation Macon, GA, USA.*

Huber shows another morphological features of its structured pigment product which is in the form of porous aggregates with high brightness (Figure 2.37). Particles are composed of stacks which form aggregates closer in shape to spherical particles.

2.1.37 LITHOPONE

Name: lithopone		CAS #: 1345-05-7
Chemical formula: ZnS·BaSO ₄		Functionality: none
Chemical composition: ZnS - 29-59%, BaSO ₄ - 70-40%, ZnO - 1%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 4.2-4.3	Mohs hardness: 3	
CHEMICAL PROPERTIES		
pH of water suspension: 7-8		
OPTICAL & ELECTRICAL PROPERTIES		
Color: white	Conductivity, mS/cm: 0.3-0.35	Brightness: 98
MORPHOLOGY		
Particle size, μm: 0.7		
Sieve analysis: 325 mesh residue - 0.004-0.02%		Specific surface area, m ² /g: 3-5
MANUFACTURER & BRAND NAME: Sachtleben Chemie, Duisburg, Germany Lithopone 30 L, 30 D, 30 DS, 60 L - the number is the percentage of ZnS, DS is micronized grade, D is the grade which is easier to disperse		
MAJOR PRODUCT APPLICATIONS: paints (used to replace up to 60% TiO ₂), coatings, thermoplastics, thermosets and paper		
MAJOR POLYMER APPLICATIONS: melamine resin, polyester, alkyd, acrylic, rubber, PP, ABS, PVC		

The advantages of lithopone when used in paints include improved weathering, algae protection, and cost reduction. Up to 60% titanium dioxide can be saved by the use of lithopone due to its excellent hiding power and brightness.

In paint reformulation, several rules must be obeyed to obtain a satisfactory result. One part of titanium dioxide is replaced by 2.5-3 parts of lithopone. The amount of extender pigment should be reduced to compensate for the increased volume of white pigment. requires about 1/3 less wetting agent because it has a lower specific surface area than titanium dioxide. The amount of binder should be reduced in such a manner that total PVC is increased by 2-5 units. The reduction of binder is a logical consequence of the increased packing density. It results in an increase of scattering coefficient. The correct level of binder reduction can be estimated from evaluation of resistance to washing and scrubbing. Finally, the water level should be adjusted to obtain the same pigment/extender/binder solids proportion in the formulation.

2.1.38 MAGNESIUM OXIDE³³²

Name: magnesium oxide		CAS #: 1309-48-4
Chemical formula: MgO	Functionality: OH	
Chemical composition: MgO - 93.72%, SiO ₂ - 2%, CaO - 3.37%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.4	Melting point, °C: 2852	
Thermal conductivity, W/mK: 8-32	Loss on ignition, %: 2.72	
Thermal expansion coefficient, 10 ⁻⁶ /K: 13		
OPTICAL PROPERTIES		
Refractive index: 1.736	Color: white	
MORPHOLOGY		
Sieve analysis: 325 mesh residue - 3%	Crystal structure: cubic	
MANUFACTURERS & BRAND NAMES: Charles B. Chrystal Co., Inc., New York, NY, USA Magnesium oxide - chemical grade for neutralization		
MAJOR PRODUCT APPLICATIONS: curing agent, acid scavenger		
MAJOR POLYMER APPLICATIONS: polyester, rubber		

2.1.39 MAGNESIUM HYDROXIDE³³³⁻³⁴¹

Name: magnesium hydroxide		CAS #: 1309-42-8
Chemical formula: Mg(OH) ₂		Functionality: OH and from surface treatment
Chemical composition: Mg(OH) ₂ - 96-98%, possible modifications by silane and fatty acids		
Trace elements: Fe, Mn, Cu		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.4	Loss on ignition, %: 30-30.5	Decomposition temp., °C: >300
Decomposition heat., kJ/g: 1.1-1.45		Decomposition peak, °C: 320-440
CHEMICAL PROPERTIES		
Chemical resistance: reactive with acids		
Moisture content, %: 0.2-1	Water solubility, %: traces	Acid soluble matter, %: 100
OPTICAL PROPERTIES		
Refractive index: 1.56-1.58	Color: white	
MORPHOLOGY		
Particle size, μm: 0.5-7.7	Crystal structure: hexagonal	
Specific surface area, m ² /g: 1-30	Oil absorption, g/100 g: 40-50	
MANUFACTURERS & BRAND NAMES: Dead Sea Bromine Group, Beer Sheva, Israel Magnesium Hydroxide FR-20 Duslo, a.s., Sala, Slovak Republic Duhor N-PL (general use and rubber and PE), C-02 (PP, PS), C-03 (EPDM, EVA), C-041(PA_6) (N-grade is untreated magnesium hydroxide and C grades are surface treated for the use in different polymers as indicated for each grade)		
MAJOR PRODUCT APPLICATIONS: cable, building industry		
MAJOR POLYMER APPLICATIONS: PA, PVC, PE, PP, EVA, nitrile rubber, HIPS, ABS		

Magnesium hydroxide is an emerging filler for fire retardant applications. In this area, it competes with aluminum trihydroxide, antimony oxide, and other fillers based on zinc. Magnesium hydroxide has a different decomposition temperature from aluminum trihydroxide, it is more suitable for polymers with higher decomposition temperature. These aspects and current findings are discussed in detail in Chapter 10.

2.1.40 METAL-CONTAINING CONDUCTIVE MATERIALS³⁴²⁻³⁴⁴

Names: nickel coated carbon fiber, steel fiber, powder, silver coated hollow and solid glass spheres, silver coated mica, silver coated fiber	
Chemical formula: composite materials	Functionality: none or derived from coating
Chemical composition: variable composition; silver coatings in Conduct-O-Fil solid glass spheres and fibers - 4-16 wt%, 30% on hollow glass spheres, 65 wt% on mica flakes, 8-19 wt% on copper flakes, 24 wt% on nickel granules, 20 wt% on aluminum particles, nickel coating on Compmat carbon fiber is 24 wt%	
PHYSICAL PROPERTIES	
Density , g/cm ³ : 2.7 (nickel coated carbon fiber Besfight MC), 3.1-3.4 (AgCLAD, silver coated thick-wall spheres), 2.7-2.9 (AgCLAD, fiber coated with silver), 0.6-0.8 (Metalite, silver coated light glass spheres); 2.5-2.8 (solid glass spheres and fibers - Conduct-O-Fil), 1.4-1.65 (hollow glass spheres - Conduct-O-Fil), 9.1-9.2 (silver coated copper products - Conduct-O-Fil), 3.1 (silver coated aluminum powder - Conduct-O-Fil), 4.8 - (silver coated inorganic flake - Conduct-O-Fil), 3.0 (nickel coated Compmat carbon fiber)	
Mohs hardness: 7 (AgCLAD, thick-walled spheres coated with silver), 5-6 (Metalite, glass light spheres coated with silver)	
Tensile strength , MPa: 3600 (Compmat)	Tensile modulus , GPa: 3600 (Compmat)
Elongation , %: 1.1-1.3 (Compmat)	Specific heat , kJ/kg·K: 0.65-1 (Compmat)
Compressive strength , MPa: 345 (AgCLAD, thick-walled spheres coated with silver), 10-20 (Metalite, light glass spheres coated with silver), 70 (Conduct-O-Fil)	
ELECTRICAL PROPERTIES	
Dry bulk resistivity , Ω·cm: 0.005-0.008 (silver-coated products of PQ), 0.0017 (silver coated solid and hollow glass spheres - Conduct-O-Fil), 0.004 (silver coated glass fiber - Conduct-O-Fil), 0.0005-0.0006 (silver coated copper powder - Conduct-O-Fil), 0.0012 (silver coated copper flake - Conduct-O-Fil), 0.0007 (silver coated aluminum sphere - Conduct-O-Fil), 0.003 (silver coated inorganic flake - Conduct-O-Fil), 0.006 (silver coated nickel granules - Conduct -O-Fil), 0.0000016 - pure silver	
Specific resistivity , Ω·cm: 7.5x10 ⁻⁵ (Besfight MC), 1.5x10 ⁻³ (Besfight HTA carbon fiber), 6x10 ⁻⁶ (Ni)	
MORPHOLOGY	
Particle size , μm: 3 (AgCLAD silver-coated, thick-wall spheres), 45-125 (Metalite, silver-coated, light glass spheres), 50 to 300 mm (Bekinox VS for conductive textiles); Conduct-O-Fil: glass spheres - 12-92, copper flakes - 10-150	
Filament diameter , μm: 6.5-33	Aspect ratio: 15 (silver-coated nickel flakes), 200-1600 (Compmat nickel coated carbon fibers)
Thickness of metal coating , μm: 0.25 (nickel in Besfight MC), silver coating thickness of Conduct-O-Fil S series - 0.05-0.27, 0.4 (nickel in Compmat MCG)	
Specific surface area , m ² /g: 0.6	
Particle thickness , μm: 1 (silver coated nickel flakes)	
MANUFACTURERS & BRAND NAMES: American Metal Fibers, Inc., Lake Bluff, IL, USA S-207, S-208 (high gauge chopped steel fibers), C-502 (copper fibers), B-401 (brass fibers) - products for brake pad applications	

continued on the next page

MANUFACTURERS & BRAND NAMES:

Anval, Inc., Rutherford, NJ, USA

Anval Metal Powder for Plastic Filler - 304, 316 (non-magnetic stainless steel), 410L, 410, 420 (magnetic stainless steel). Spherical particles obtained by gas atomization of alloys containing different proportions of Cr, Ni, Mo, and Fe. Obtained spherical particles are classified to the required sizes. Materials can be produced to the required size in a range from 15 to 1000 μm .

Bekaert Steel Wire Corporation, Marietta, GA, USA

Bekinox VS (steel fiber), LT (steel mixed with PA), LTW & W (steel mixed with wool), Pes 12/50 (steel mixed with polyester)

Beki-Shield - steel fibers for EMI protection of plastics

Bekitex - metal-containing yarns for conductive textiles

Composite Material L.L.C., Mamaroneck, NY, USA

Compmat - nickel and copper plated graphite fiber roving, chopped fibers of different length in the range of 3 to 25 mm, and prepregs of these fibers for PA, PVA, PP, PE, polyoxazoline, Kynar, PC, ABS, HIPS, PPO, polyvinylpyrrolidone. The fibers are designed for EMI/RFI shielding

Inco Europe Ltd., Swansea, UK

VaporFab - nickel coated carbon fiber by a chemical vapor deposition process for EMI shielding applications

IncoShield - concentrates of nickel-coated carbon fiber in PPS, PC, PMMA, PEI, PA-6, PA-12.

Concentrates are used for production of conductive polymers

JB Company, Franklin, NJ, USA

Glass Beads Silver and Gold - metallized beads for decorative applications

MO-SCI Corporation, Rolla, MO, USA

MetaSpheres - glass microspheres coated with Ni, Co, Cu, Ag, Au, Pd, Pt, Rh. Typical coating thickness 2%.

Novamet Specialty Products Corporation, Wyckoff, NJ, USA

Novamet Silver-coated Nickel Flakes - for conductive materials

Novamet Nickel Coated Graphite-60 - graphite powder coated with metal for EMI shielding applications

Plastic Methods Co., Inc., New York, NY, USA

CMC Cathospheres - coppers, nickel, gold, and silver coated glass spheres of diameter sizes from 1.1 to 14 mm, designed for barrel plating which eliminates rack plating

Potters Industries Inc., Affiliate of the PQ Corporation, Valley Forge, PA, USA

Conduct-O-Fil S series - silver coated solid glass spheres. Twelve grades in particle sizes range of 12-92 μm . Materials for conductive adhesives, caulks, coatings, elastomers, greases, inks

Conduct-O-Fil SH - silver coated hollow borosilicate glass spheres containing 30 wt% silver

Conduct-O-Fil SM - silver coated mica flake

Conduct-O-Fil SC - silver coated copper; SC230F8, SC500F20, SC140F19 - flakes, SC325P17

- granules, SC500P18 - powder

Conduct-O-Fil SN - silver coated nickel granules

Conduct-O-Fil SA - silver coated aluminum particles

Conduct-O-Fil PI-1040 - aluminum compatible particles which do not cause galvanic corrosion in gaskets contacted with aluminum

The PQ Corporation, Valley Forge, PA, USA

AgCLAD TW and Filament 32 - a thick-walled spheres and fiber coated with silver, respectively

Metalite SG, CG, SF-20 - light hollow glass spheres coated with silver

Toho Rayon Co., Ltd, Tokyo, Japan

Besfight MC and HTA-CF - carbon fiber nickel-coated with excellent mechanical properties of carbon fiber and good electric conductivity of nickel. The material for conductive plastics.

MAJOR PRODUCT APPLICATIONS: adhesives, caulks, sealants, inks, paints, coatings, EMI control, gaskets, decoration, plating, composites, building products, computers, pastes for electronics, stucco, arts and crafts, smoke detectors, covers, printers, copiers

MAJOR POLYMER APPLICATIONS: thermosets, silicones, polyurethanes, epoxy, acrylics, PP, PPS, PC, ABS, PEI, PA

This section discusses conductive materials. Although, not consistent with chapter organization, all materials which are composed of two different materials or are in the form of conductive fibers have been included here for easier comparison. Other metallic materials, if they are composed of a single metal, can be found in other sections. Metal coated spheres, flakes, and fibers are manufactured for various applications. Conductive plastics are the most common. Nickel-coated graphite fibers were developed in the 1980s by American Cyanamid. These fibers combine the strength of fiber with the electrical and thermal conductivities of nickel. The choice of nickel is dictated by the fact that it is a relatively inexpensive metal with good corrosion resistance. Typically, 3-5% fibers in material give the static dissipating properties. Toho Rayon, Co. further improved the performance of the material by the use of their technology of carbon fiber manufacturing and a very precise coating of a thin layers of nickel. Figure 2.38 shows the morphology of surface and the cross-section of these fibers from two manufacturers: Toho Rayon, Co. and Composite Materials, L.L.C. The specific resistivity of nickel coated fibers is only one order of magnitude higher than nickel but two orders of magnitude lower than uncoated fiber.

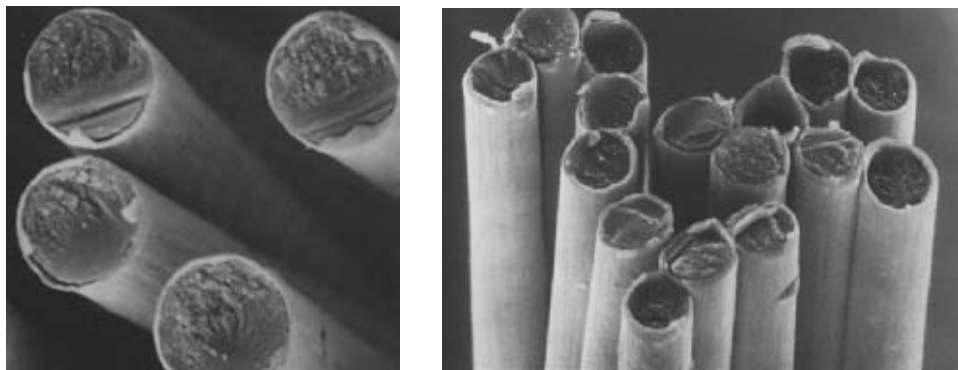


Figure 2.38. SEM micrograph of nickel coated carbon fiber (left - Besficht, Toho Rayon, Co.) (right - Compmat, Composite Materials). *Courtesy of Toho Rayon, Co., Tokyo, Japan and Composite Materials, L.L.C, Mamaroneck, NY, USA.*

Other substrates such as graphite powder and mica are also coated with nickel. Silver is the most conductive metal, being almost 5 times less resistant than nickel. Silver and copper have very similar conductivities but copper is easily oxidized and reacts with acids readily which affects its performance in polymeric systems. The PQ Corporation and Potters Industries, Inc. have developed a whole range of products which are silver coated. Their application is for conductive thermosets, gaskets, sealants, adhesives, paints, coatings, inks, and EMI control applications. Its use in these products saves 1/3 of weight of conductive material.

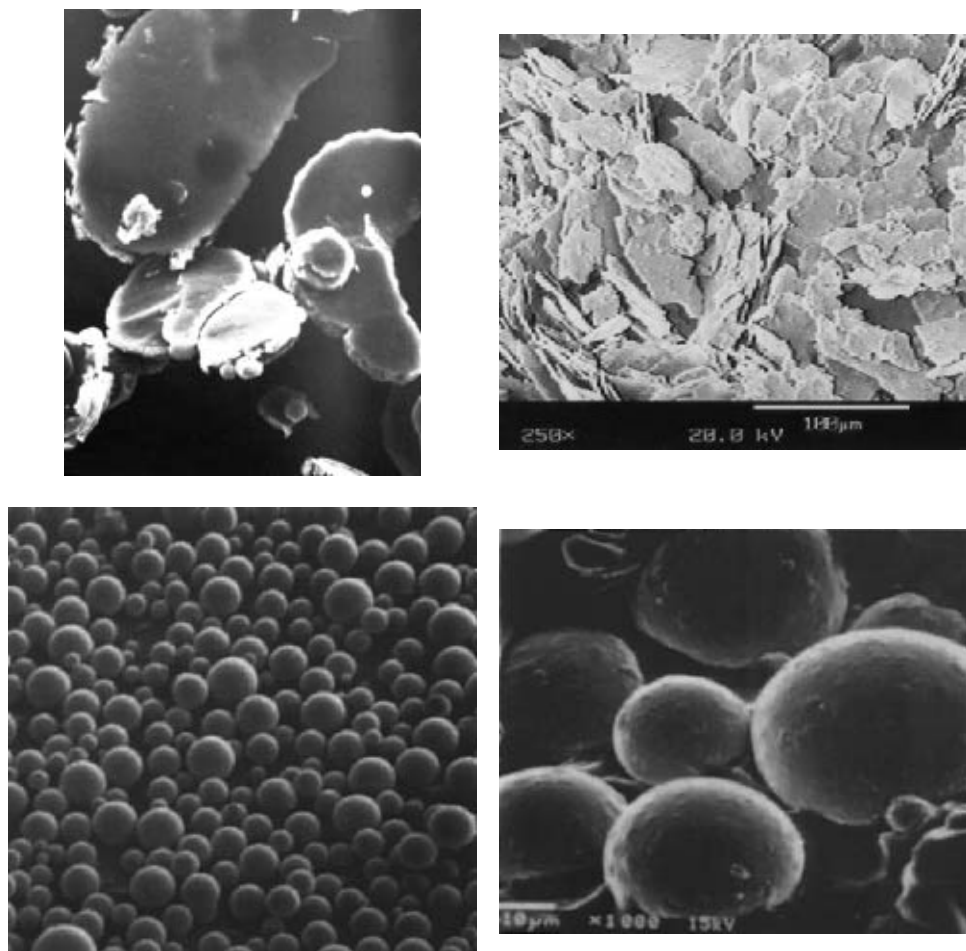


Figure 2.39. SEM micrographs of silver-coated flakes and spheres. Upper left - Novamet' silver coated nickel flakes, upper right - Conduct-O-Fil SC230F8, silver coated copper flakes, bottom - Conduct-O-Fil solid glass spheres coated with silver, left - spheres at 100x magnification, right - spheres in silicon resin. *Courtesy of Novamet Specialty Product Corporation, Wyckoff, NJ, USA and Potters Industries, Inc., Valley Forge, PA, USA.*

Novamet developed a concept to improve the properties of nickel flakes by coating them with 15% silver. The coated flakes have both conductivity and ferromagnetic properties. In addition, because of the differences in density ($\text{Ag} - 10.5$ and $\text{Ni} - 8.9 \text{ g/cm}^3$), it is possible to save 15% in material since conductivity is related to volume rather than to weight and surface conductivity is usually of primary importance. Figure 2.39 shows the morphology of several conductive materials. Metal flakes from silver coated nickel and copper flakes have irregular shapes because they are formed from spherical particles which were first coated with silver and then flattened by mechanical forces. The apparent difference in

thickness between the two products is due to the different magnifications. Both products have a similar thicknesses of about 1 μm . Coating consistency is essential since silver must play the role of the corrosion protective metal for copper (nickel is corrosion resistant). The consistency of the silver layer depends, in addition to the conditions of the process, on the properties of the metals involved and on the adhesion between layers. The morphology of spherical particles does not differ from uncoated glass spheres. It can be noted from the micrograph on the right side that spheres have excellent adhesion to silicon resin.

Potters Industries, Inc. developed a new aluminum compatible particles which can be used in gaskets in contact with aluminum. If silver in the gasket were to come in contact with the aluminum of the enclosure, galvanic corrosion may result. The aluminum compatible grade was found to pass 3000 hours in a salt spray chamber without loss of shielding effectiveness.

Plastic Methods Co., Inc. found an interesting application for metal coated glass spheres. The spheres are mixed with a product to be plated or burnished. The balls are light and perfectly round therefore they do not damage the material surface and provide excellent conductivity for even metal distribution in semi-conductor parts and jewelry.

JB Company manufactures glass beads coated with metal for decorative purposes.

2.1.41 MICA³⁴⁵⁻³⁶¹

Name: mica		CAS #: 1318-94-1, 12001-26-2
Chemical formula: $AB_{2-3}(Al,Si)Si_3O_{10}(OH)_2$ A=K, Na, Ca, Ba; B=Al, Fe, Mg, Li; muscovite: $KAl_2(AlSi_3O_{10})(OH)_2$, phlogopite: $KMg_3(AlSi_3O_{10})(OH)_2$		Functionality: OH
Chemical composition: muscovite: SiO_2 - 44-48%, Al_2O_3 - 31-38%, K_2O - 3-11%, Fe_2O_3 - <1-5.7%; phlogopite: SiO_2 - 40-42%, MgO - 21-24%, Al_2O_3 - 9-16%, Fe_2O_3 - 9-11%, K_2O - 10-11%		
PHYSICAL PROPERTIES (M) - muscovite mica, (P) - phlogopite mica; most data in this table courtesy of <i>Polar Minerals</i> , Mt. Vernon, IN, USA		
Density, g/cm ³ : 2.75-3.2 (M), 2.74-2.95 (P)		Mohs hardness: 2.5-4 (M), 2.5-3 (P)
Decomposition temp., °C: 1300 (P)		Loss on ignition, %: 4-9 (M), 2 (P)
Maximum temperature of use, °C: 500-530 (M), 850-1000 (P)		Specific heat, kJ/kg · K: 0.21
Linear coefficient of thermal expansion, 1/°C: $1.5-25 \times 10^{-6}$ (M), $1-1000 \times 10^{-6}$ (1 to cleavage); $9-80 \times 10^{-6}$ (M), $13-14.5 \times 10^{-6}$ (P) (11 to cleavage)		
Tensile strength, MPa: 250-860	Tensile modulus, MPa: 172,000	Compressive strength, MPa: 220
Coefficient of friction: 0.1-0.2 (M), 0.2-0.4 (P)		
CHEMICAL PROPERTIES		
Chemical resistance: very good (M), good (P)		
Moisture content, %: 0.3-0.7	Water of constitution, %: 4.5 (M), 3.2 (P)	
pH of water suspension: 6.5-8.5 (M), 7-8.5 (P)		
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 1.55-1.61 (M), 1.54-1.69 (P)		Reflectance: 87 (M) 42-64 (P)
Color: white, off-white to beige (M), golden brown to bronze (P)		Brightness: 55-65
Dissipation factor: $4.5-8.2 \times 10^{-2}$	Loss tangent: 0.0013 (M), 0.02-0.04 (P)	
Dielectric constant: 6.5-9 (M), 5-7 (P)	Dielectric strength, V/cm: 7-15 (M), 5-10 (P)	
Specific resistivity, Ω-cm: $10^{12}-10^{16}$ (M), $10^{10}-10^{13}$ (P)		Power factor: 0.08-0.09
MORPHOLOGY		
Particle shape: hexagonal	Crystal structure: monoclinic	Cleavage: basal
Particle size, μm: 4-70	Oil absorption, g/100 g: 65-72	
Aspect ratio: 10-70	Particle thickness, μm: 1.1-2.6	
Sieve analysis: 325 mesh residue - 1-45%		

MANUFACTURERS & BRAND NAMES:

Asheville Mica Company, Newport News, VA, USA

Mica 325, 325FF, 325MF, 325D, AMC, 160 D - dry ground mica for rubber applications.

Aspect Minerals (Zemex), Spruce Pine, NC, USA

AlbaFlex (25, 50, 100, 200, 300, 400), AlbaShield (15, 20, 25, 25-S, 50, 50-S, 1000, 2000) - wet ground muscovite micas

AFlake - ground mica flakes

Cosmetic line for the use in lipstick, face powder, eyeshadow, and nail polish

Surface treated mica

Franklin Industrial Minerals, Kings Mountain, NC, USA

WG-325, HiMod-270, HAR-160, WG-160, H-160 - wet ground muscovite mica

19 grades of dry ground muscovite mica in particle sizes from 17 to 550 μm

Les Produits Mica Suzorite, Inc. (Zemex), Boucherville, PQ, Canada

15-Z, 20-S, 25-Z, 40-S, 40-Z, 50-SD, 60-HK, 60-PE, 60-PO, 60-PP, 60-S, 60-Z, 80-SF, 150-NY,

150-S, 200-HK, 200-PE, 200-PP, 200-S, 325-HK, 325, PE, 325-PO, 325-PP, 325-S,

(SD, Z - purposely not fully delaminated or purified, HK - highly or super-delaminated,

SF and S - highly delaminated, PE, PO and PP - surface treated)

Mica-Tek, Northville, MI, USA

Mica-Lyte, Dekorflake, Microfibers, Specular - selected natural, colored, and shaped materials designed as special-effect colorants to impart granite-like, sparkling, and textured appearances to transparent and translucent polymers

Non-Metals, Inc., Affiliate of The China National Non-Metallic Minerals Group, Tucson, AZ, USA

Muscovite Mica Powder - D Series (dry ground), W Series (wet ground)

Polar Minerals, Mt. Vernon, IN, USA

Phlogopite Mica 5200(s), 5100(s), 5040(s), 5010(s) - grades having different particle sizes; (s) means that the product can be supplied with chemical coating

Muscovite Mica 6915, 6912, 6908, 6905 - grades of different particles sizes for plastics and coatings

SG-70, SG-90 - hydrous potassium aluminum silicate produced by patented process which gives high brightness delaminated muscovite mica for joint compounds, adhesives, sealants, coatings

MAJOR PRODUCT APPLICATIONS: paints, coatings, composites, plastic parts, sound dampening, foundry coating, lipsticks, face powders, eyeshadows, nail polish, mold release agents, bathwares, housewares, toys, interior decoration, asbestos substitute, filtration aids, asphalt-based compounds and coatings, drilling fluids, insulating heat shields, gaskets, gypsum board, tank linings

MAJOR POLYMER APPLICATIONS: ABS, PP, PA, PC, PMP, PE, PET, PBT, PMMA, PS, PVC, rubber

The mica group has about 30 members but only a few are common. Muscovite, phlogopite, and biotite are important representatives of this group. Muscovite is one of the most common of the micas and occurs in a wide variety of geological environments because of its stability. Crystals measuring 2-3 m across are mined in some locations. Muscovite can vary in chemical composition as a result of atomic substitution (Na for K; Mg and F for Al).

Phlogopite is found in metamorphosed magnesium-rich limestones, dolomites, and ultrabasic rocks. Biotite, similar to muscovite, is also widespread. It is usually associated with minerals which were formed under high temperature and pressure. Several elements, other than those included in their typical chemical composition, can be found in these two minerals. These include: Na, Rb, Cs, Ba, F, and Ca. The most important difference between phlogopite and biotite is that biotite contains a substantial amount of iron.

Of the three micas characterized above, muscovite and phlogopite are the most commonly used. Muscovite is almost colorless, phlogopite has a golden brown

color, whereas biotite is black. The color influences mica application to a great extent, and practically speaking, muscovite and phlogopite are the only minerals used, with muscovite being the more popular.

Mica fillers are obtained by separation of mica from other minerals which might compose 10-20% of mineral content. Mica is dry or wet milled and classified. The mechanical grinding produces flakes with a low aspect ratio in a range from 20 to 40. The process may include ultrasonic delamination which leads to a high aspect ratio of over 200. Flakes of mica fillers have a thickness in a range from 1 to 3 μm and a width in a range from 10 to 450 μm .

A high aspect ratio contributes greatly to polymer reinforcement, and also allows production of highly-filled polymers. For this reason the aspect ratio should be regarded as the most important single property characterizing the quality of micas. The technology of mica filler manufacture may include surface preparation using silanes, maleated polypropylene wax, and amine acetate. These processes greatly enhance reinforcement. Ultrasonic delamination especially becomes more effective when surface treatment is used. This is related to increased mica wetting, which is usually difficult compared to other fillers. Surface coupling also greatly affects the resistance of the filled polymer to water – one of the most desired mica properties when it is compared with other fillers.

For some applications it is essential to control the concentration of iron which may vary over a broad range, regardless of mineral type. There are muscovite types known to contain up to 5% of Fe_2O_3 (although it would be expected to contain none), whereas biotite may contain as little as 2% of Fe_2O_3 (it typically contains iron in its chemical formula).

Other reasons are known for mica's frequent use: one, of long standing tradition in the industry, is related to its high resistivity; the other is its effect on thermal expansion. Composites including mica have a low coefficient of thermal expansion comparable to those including glass flakes. In addition, mica is used to reduce shrinkage, warpage, and to improve tensile strength and modulus, high temperature deflection, and permeability.

Mica-Tek has an interesting approach to exploiting the variety of forms and colors of mica. A range of mica-based products have been developed which differ in the color and the shape of particle as well as in their glittering and sparkling effects. These decorative pigments are used in housewares, bathwares, toys, interior decorating, etc.

Figure 2.40 shows SEM micrographs of muscovite and phlogopite mica. The morphological features of both forms are very similar.

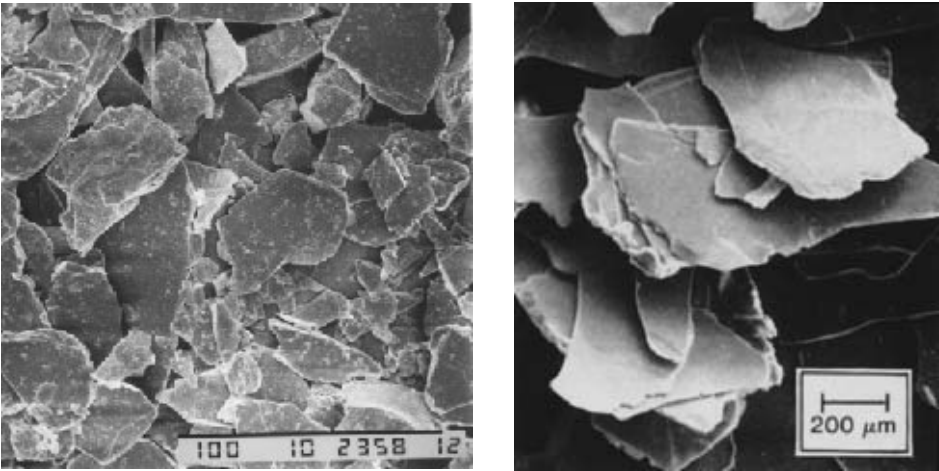


Figure 2.40. The morphology of muscovite (left) and phlogopite (right) mica. *Courtesy of NYCO, Minerals, Inc., Willsboro, NY, USA (muscovite) and Les Produits Mica Suzorite, Inc., Boucherville, PQ, Canada.*

2.1.42 MOLYBDENUM

Name: molybdenum powder		CAS #: 7439-98-7
Chemical formula: Mo	Functionality: none	
Chemical composition: Mo - 99-99.99%		
Trace elements: O - 600-1000 ppm		
PHYSICAL PROPERTIES		
Density, g/cm³: 10.2	Melting point, °C: 2610	
CHEMICAL PROPERTIES		
Chemical resistance: soluble in concentrated strong acids		
MORPHOLOGY		
Particle size, µm: 1-50	Crystal structure: cubic	
MANUFACTURER & BRAND NAMES: CSM Industries, Coldwater, MI, USA OMP - high purity, fine powder obtained from molybdenum trioxide which is hydrogen reduced. It is composed of agglomerated particles MMP highest purity powder produced from ammonium dimolybdate and it is hydrogen reduced and agglomerated, deagglomerated powders are also available SOMP, PDMP - spherically shaped particles produced by spray drying, atomization, and plasma densification are flowable powders		
MAJOR PRODUCT APPLICATIONS: electronics, aerospace		

Figure 2.41 shows an individual particle of molybdenum powder and the agglomerated powder. Spherical particles with a porous structure can be produced from agglomerates (SOMP). PDMP are also spherical particles which have a smooth surface. The agglomerated powder is composed of cubical and elongated particles.

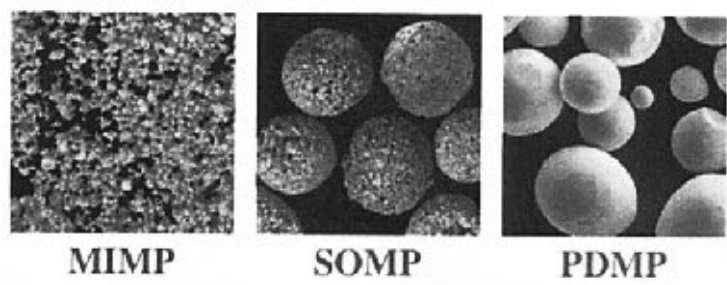


Figure 2.41. SEM micrographs of different grades of molybdenum powder. Courtesy of CSM Industries, Coldwater, MI, USA.

2.1.43 MOLYBDENUM DISULFIDE³⁶²⁻³⁶⁶

Name: molybdenum disulfide		CAS #: 1317-33-5
Chemical formula: MoS ₂	Functionality: S	
Chemical composition: MoS ₂ - 98%		
Trace elements: Fe, O		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 4.8-5	Mohs hardness: 1	Melting point, °C: 1600 (decomp)
Thermal conductivity, W/K · m: 0.13-0.19	Coefficient of thermal expansion, 1/°C: 10.7x10 ⁻⁶	
Coefficient of friction: 0.03-0.06		
CHEMICAL PROPERTIES		
Acid soluble matter, %: 95.5		
MORPHOLOGY		
Particle size, μm: 0.4-38		
MANUFACTURERS & BRAND NAMES: AML Industries, Inc., Warren, OH, USA Amlube 510 - technical grade, 511 - fine technical grade Climax Molybdenum Company, Ypsilanti, MI, USA Technical, Technical Fine, Super Fine (Suspension) - grades having different particle sizes EM Corporation, West Lafayette, IN, USA E-4 - purified molybdenum disulfide powder Parma-Slik - mixtures of molybdenum disulfide and graphite		
MAJOR PRODUCT APPLICATIONS: plastic parts (e.g., piston rings, cams, ball bearing retainers, space shuttle bearings, etc.), greases, lubricating aerosols, oil additives, metalworking compounds		
MAJOR POLYMER APPLICATIONS: PA, PTFE, phenoxy, epoxy, PC, polyarylate		

The compound occurs as the mineral molybdenite which after refining is also used as lubricating material. The principle of action of molybdenum sulfide is based on



Figure 2.42. SEM micrograph of molybdenum disulfide. Courtesy of Climax Molybdenum Company, Ypsilanti, MI, USA.

the formation of bonds between metal and sulfur. These bonds slip under shear forces and are continuously re-formed holding the lubricating film on the surface of the metal.

Figure 2.42 shows morphology of technical grade of molybdenum disulfide.

2.1.44 NICKEL³⁶⁷⁻³⁷⁰

Names: nickel		CAS #: 7440-02-0
Chemical formula: Ni		Functionality: none
Chemical composition: Ni - >99%, C- 0.1-0.25%		
Trace elements: Fe, O		
PHYSICAL PROPERTIES		
Density, g/cm³: 8.9	Specific heat, kJ/kg · K: 0.44	Melting point, °C: 1455
Thermal conductivity, W/K · m: 158	Coefficient of thermal expansion, 1/°C: 13x10 ⁻³	
ELECTRICAL PROPERTIES		
Resistivity, Ω-cm: 7.8x10 ⁻⁶		
MORPHOLOGY		
Particle size, µm: 2.2-9	Aspect ratio: 15-50	
Particle thickness (flakes), µm: 0.4-1.3	Specific surface area, m²/g: 0.6-0.7	
Sieve analysis: 325 mesh residue: 1-4%		
MANUFACTURERS & BRAND NAMES: INCO Specialty Powder Products, London, UK and AcuPowder International, Union, NJ, USA INCO Nickel Powder Type 123 - powder metallurgy INCO Filamentary Nickel Powder Types 255, 270, 287 - plastics and electronics Novamet Specialty Products Corporation, Wyckoff, NJ, USA Nickel Flake Powder - leafing and water grade products for protective paints (both grades can be used in solvent-based systems) Conductive Nickel Flake Powder HCA-1 - product developed for conductive paints and adhesives which provides EMI shielding when used in surface coatings, inks, and adhesives. The flakes are treated in a controlled atmosphere to give cleaner surface which enhances conductivity Conductive Nickel Pigment 525 - dendritic filamentary shape similar to INCO products CNS - spherical shape and uniforms size for thick film inks		
MAJOR PRODUCT APPLICATIONS: EMI/RFI shielding, powder coating, anti-size lubricants, decorative lacquers, waterborne coatings, conductive plastics, non-stick coatings, coatings for cookware, adhesives, inks, sealants		
MAJOR POLYMER APPLICATIONS: silicone, polyurethanes, epoxy, PE, PP		

Nickel in addition to being highly conductive has ferromagnetic properties and it is a relatively inert material. INCO produces nickel powders by thermal decomposition of nickel carbonyl in a process which produces a fine particle metal powder with a spiked or dendritic surface (Figure 2.43). The micrograph on the left hand side shows a singular particle of grade 123. The morphology of Types 255, 270, and 287 is shown in the figure on the right hand side. The dendritic particles are connected to each other to form a chain of a controlled length and porosity.

Figures 2.44 and 2.45 show the morphology of two grades produced by Novamet: flake powder and spherical material.

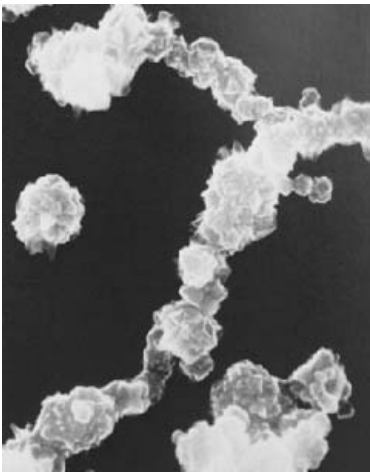


Figure 2.43. INCO nickel powder single particle (left) and chain (right). *Courtesy of INCO Specialty Powder Products, London, UK.*

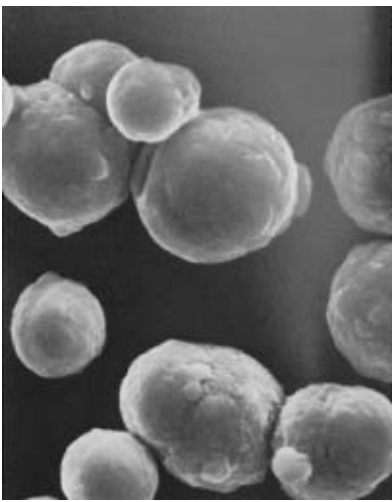
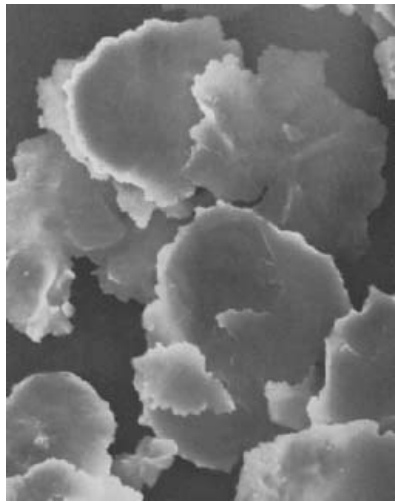


Figure 2.44. Novamet nickel flakes. *Courtesy of Novamet Specialty Products Corporation, Wyckoff, NJ, USA.*

Figure 2.45. Novamet spherical nickel, CNS. *Courtesy of Novamet Specialty Products Corporation, Wyckoff, NJ, USA.*

2.1.45 PERLITE³⁷¹

Name: perlite		CAS #: 93763-70-3
Chemical formula: depends on the rock composition		Functionality: OH and silane functionality
Chemical composition: SiO ₂ - 71-75%, Al ₂ O ₃ - 12-18%, Na ₂ O - 3-4%, K ₂ O - 4-5%, Fe ₂ O ₃ - 0.5-1.5%, MgO - 0.1-1.5%		
Trace elements: Mn, Ti		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 1.2-2.4	Mohs hardness: 5.5	Loss on ignition, %: 1.5
Specific heat, kJ/kg·K: 0.88	Softening point, °C: 871	Expansion temperature, °C: 871
CHEMICAL PROPERTIES		
Chemical resistance: soluble in hot alkalis and strong acids		Water solubility, %: 1
Moisture content, %: 0.5-1	pH of water suspension: 5.5-8.5	Acid soluble matter, %: 3
OPTICAL PROPERTIES		
Refractive index: 1.5	Brightness: 74	
Color: off-white		
MORPHOLOGY		
Particle shape: irregular flake	Particle size, μm: 11-37	Oil absorption, g/100 g: 210-240
Specific surface area, m ² /g: 1.88		
MANUFACTURERS & BRAND NAMES: Grefco, Inc., Lompoc, CA, USA FF1, FF26, FF36, FF56, FF76 - grades of different particles sizes. FF56 and FF76 have very low effective density of 1.2-1.3 g/cm ³ . All grades are available with surface modification Strong-Lite Products Corporation, Pine Bluff, AR, USA range of perlite grades mostly for construction and horticulture		
MAJOR PRODUCT APPLICATIONS: construction (thermal insulation, concrete, under-floor insulation), paints, horticulture, filtering, mild abrasives, filler of plastics, caulks, explosives, carrier of agrochemicals		
MAJOR POLYMER APPLICATIONS: PE, PP, PVC		

Perlite is a volcanic rock found in many locations. If rapidly heated to 871°C it expands up to 20 times. Figure 2.46 shows the morphology of Perlite FF-56 which is very light filler.

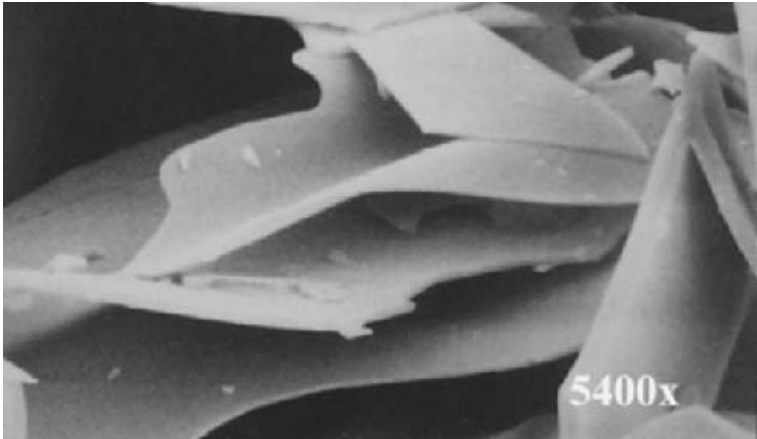


Figure 2.46 SEM micrographs of Perlite FF-56. *Courtesy of Grefco, Inc., Lompoc, CA, USA.*

2.1.46 POLYMERIC FILLERS³⁷²⁻³⁸¹

Names: plastic microspheres, expandable microspheres, PTFE, PE, PI	
Chemical formula: this diverse group includes particular materials of different chemical composition which are used as functional fillers	
PHYSICAL PROPERTIES	
Density, g/cm³: Expancel microspheres: unexpanded - 1.05-1.2, expanded - 0.03-0.07; Dualite: 0.065-0.13; PTFE: 2.2; Vistamer HD & UH - 0.94-0.96, Ti - 1.58-2.44	
Melting point, °C: 329-332 (PTFE)	Coefficient of friction: PTFE - <0.1
CHEMICAL PROPERTIES	
Moisture content, %: Expancel - 1, Dualite - 2	
MORPHOLOGY	
Particle size, µm: Expancel: unexpanded - 6-35, expanded - 15-80; Dualite - 25-140; PTFE: 5-25 (primary particle in Algoflon - 0.15-0.3); Vistamer: 18-290	
Specific surface area, m²/g: PTFE: 2.5-9	
MANUFACTURERS & BRAND NAMES:	
AKZO Nobel, Expancel, Inc., Duluth, GA, USA and Sundsvall, Sweden Unexpanded microspheres 820, 643, 551, 461, 051, 053, 054, 091, 092 hollow particles with thermoplastic shell encapsulating a gas available in wet (WU) and dry (DU) form. The grade numbers signify materials which have different particle diameter, expansion rate, solvent resistance, and temperature of expansion. Expanded microspheres 551, 461, and 091 expanded hollow particles available in wet (WE) and dry (DE) forms. There also grades of the same type of shell but in different dimensions. The lines differ in particle diameter, density, and solvent resistance The shell of these microspheres is composed of vinylidene chloride and acrylonitrile copolymer	
Ausimont USA, Inc., Montedison Group, Thorofare, NJ, USA Algoflon L203, L205, L206 - micronized PTFE powders for applications in thermoplastic and thermosetting resins, printing inks, paints, oils and greases, and rubber. The lower the number the smaller the particle size. Polymist F-5, F-5A, F-5A EX, F-510, XPH-284 free-flowing PTFE powders for applications in thermoplastic and thermosetting resins, printing inks, paints, oils and greases, and rubber. The lower the number the smaller the particle size. The XPH 284 is in compliance with FDA regulation 21 CFR 177.1550 and it is recommended for articles intended for use in contact with food.	
Composite Particles, Inc., Allentown, PA, USA Vistamer HP and UH - HDPE and UHMWPE powders, respectively, with modified surface Vistamer Ti-911x, Ti-912x surface activated powders of UHMWPE and polyimide, respectively	
Pierce & Stevens Corporation, Buffalo, NY, USA Dualite M6001AE, M6033AE, M6050AE, MS7000 - low density microspheres. Grade M6001A has shell composed of poly(vinylidene chloride) copolymer. All other grades have the shells composed of acrylonitrile copolymer. All grades have calcium carbonate coating. The difference between grades is in particle size, solvent resistance, temperature resistance, and density. Grade composed of poly(vinylidene chloride) copolymer is less resistant to heat and solvent. Micropearl F-30, F-50, F-80, F100 - expandable microspheres available in wet and dry forms. These microspheres are marketed for Matsumoto Yushi-Seiyaku, Co., Ltd. Japan	
<i>continued on the next page</i>	

<p>MANUFACTURERS & BRAND NAMES: Sekisui Plastics Co., Ltd., Tokyo, Japan</p> <p>Techpolymer microspheres manufactured from acrylic and styrenic copolymers in various forms included non-crosslinked, crosslinked, porous and composite. Several manufacturing grades are designed for paints, inks, as resin-modifying agent, delustering, anti-blocking agent, and filler for toiletries and cosmetics</p> <p>Apamicon beads are of inorganic origin (hydroxyapatite) which have affinity to living organisms and are used in medical applications</p>
<p>MAJOR PRODUCT APPLICATIONS: <i>Expancel</i>: cultured marble and wood, coatings and sealants, auto and marine fillers, composites, pultruded parts, paints, crack fillers, underbody coatings, elastomer fillers, syntactic foams, cable fillings, explosives, gypsum board, printing inks, paper, paperboard; <i>Dualite</i>: boats, automotive components, tub/shower products, automotive underbody coatings, paints, adhesives, sealants, truck caps, side panels, van tops, recreational vehicles, sporting equipment, boats, PVC foam, printing inks, putties, synthetic wood, rubber products, wall papers, non-wovens, molded plastics; <i>PTFE powders</i>: broad range of products for thermoplastics and thermosetting resins, paints, coatings, printing inks, oils, greases; <i>Vistamer grades</i>: molded parts, adhesives, sealants, paints, coatings, machine parts, pump impellers, valve seats, gears, rings, bearings, liners, wear-plates, guide-rails, cable, steel replacement</p>
<p>MAJOR POLYMER APPLICATIONS: <i>microspheres</i>: PVC, polyurethanes, polyester, silicone, acrylics, epoxy, rubber; <i>PTFE powders</i>: PA, POM, PC, polyesters, PI, PSF, PSO, PPS, polyurethanes, ECTFE, EPDM, SBR, fluorosilicones, NR</p>

Expancel have developed polymeric microspheres which are widely used in various applications. The microsphere's shell is composed of vinylidene chloride and acrylonitrile copolymer and the blowing agent is isobutane. Increasing temperature softens shell and expands gas which at a certain temperature has sufficient pressure to expand the shell. The temperature of expansion is characteristic of the grade but it also depends on the matrix in which Expancel is dispersed. Typically, expansion begins at temperatures form 75 to 135°C and ends between 115 to 195°C depending on the grade of filler. The expansion rate depends on the process conditions. The microspheres can reach up to 50 times of their initial volume. The unexpanded microspheres can be used as a foaming or blowing agents. The expanded microspheres form an ultralow density modifier which does not greatly increase viscosity.

Expanded microspheres maintain their density even after a prolonged heating at temperature range of 140-160°C. Also compression at high pressures (150 bar) does not change the density of the expanded material. In any new formulation, Expancel needs to be checked for the compatibility with the other components of the system. In particular, it should be established whether the microspheres are resistant to the liquids in formulation, such as solvents, plasticizers, curatives, etc. The mixing process is complicated by the fact that microspheres, especially in the pre-expanded form, have a much lower density than the other components of the formulation therefore they float the surface of the mixture which creates difficulties in incorporation and creates the potential for their loss to the surrounding air. Microspheres have good mechanical resistance and can be mixed by high shear mixers. Also, vacuum does not affect microspheres. If mechanical resistance is of

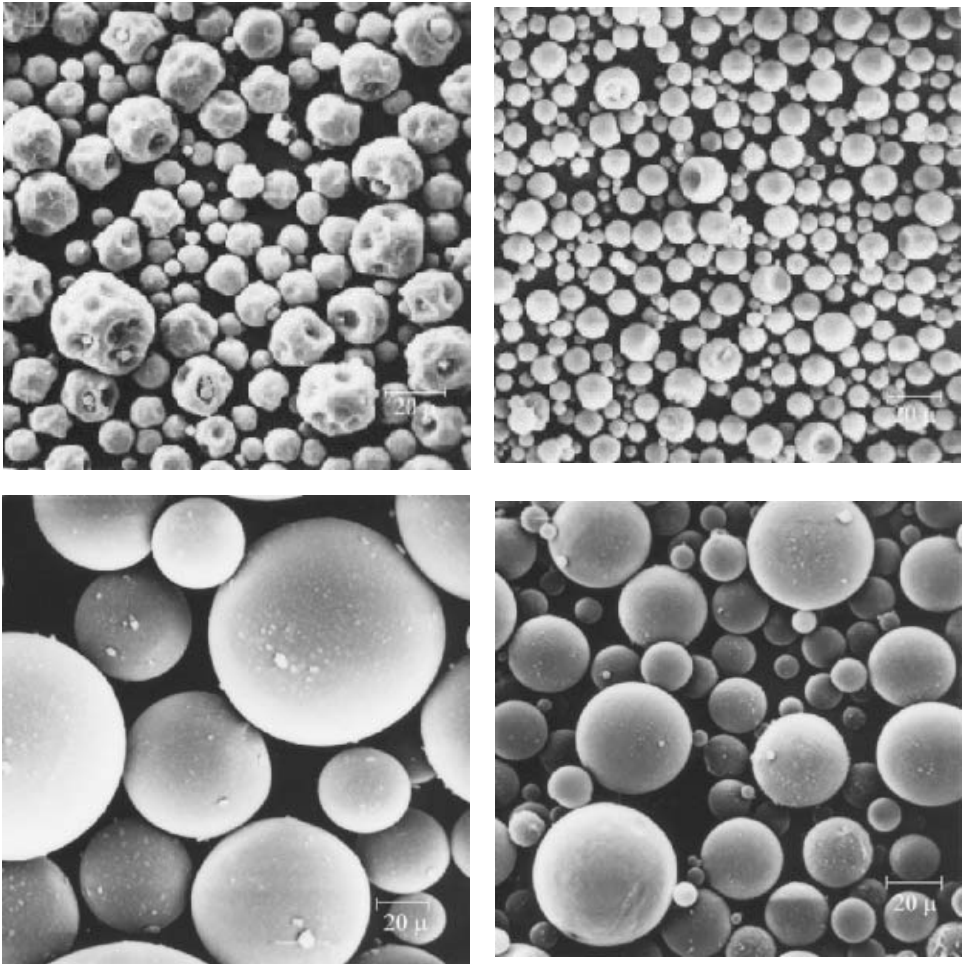


Figure 2.47. Expancel 551 (left) and 091 (right). The top micrograph - unexpanded, the bottom - expanded. Courtesy of AKZO Nobel, Expancel, Inc., Duluth, GA, USA.

concern, DU grades should be selected since they are smaller and have thicker walls.

Figure 2.47 shows the morphology of two grades before and after expansion. The 551 grade has more spherical particles before expansion because they have a thicker shell and they will expand to a higher density than the 091 grade. But after expansion both grades form perfectly spherical particles.

A close inspection of micrographs in Figure 2.47 shows that there are small particles attached to the surfaces of microspheres which form surface imperfections. The Figure 2.48 shows a new grade 007 which has very clean surface.

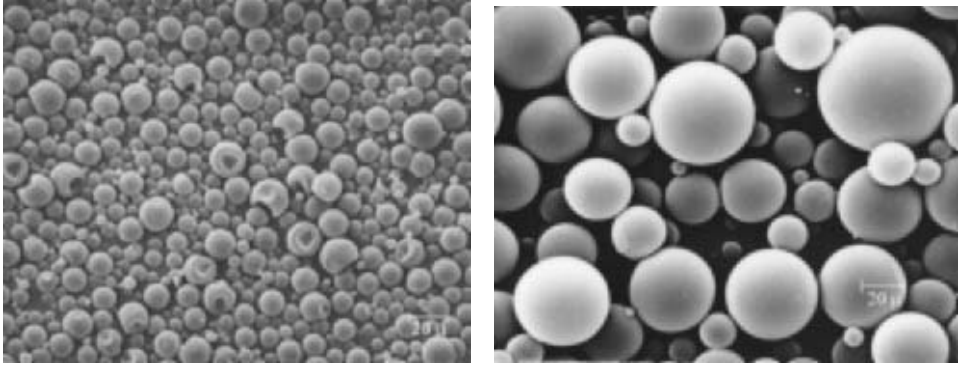


Figure 2.48. Expancel 007 before and after expansion. *Courtesy of AKZO Nobel, Expancel, Inc., Duluth, GA, USA.*

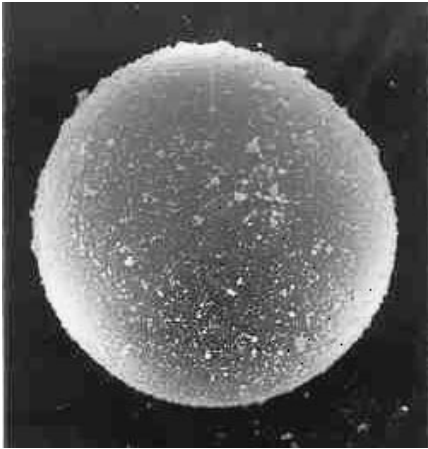


Figure 2.49. SEM micrograph of Dualite microsphere. *Courtesy of Pierce & Stevens, Buffalo, NY, USA.*

Pierce & Stevens Corporation patented the concept of manufacturing polymeric beads with a calcium carbonate coating which is inert and compatible with many materials in which microspheres are dispersed. Figure 2.49 shows individual particle of Dualite which has similar morphological features to other polymeric microspheres in spite of the fact that the surface is coated with calcium carbonate. This shows that the process is capable producing this complex composite with a high degree of precision. Also, particle size distribution curves show a narrow distribution indicating good control over processing. These microspheres resist high shear dispersion, vacuum, pressure, heat and are not affected by methyl ethyl

ketone (acrylonitrile shell). The published papers³⁷⁷⁻³⁷⁹ give guidelines regarding the application of microspheres in composites, surface finishes, coatings, sealants and adhesives.

Polytetrafluoroethylene powders have found a large number of applications due to their lubricating properties, chemical inertness, improvement to wear characteristics, reduction of the friction coefficient, resistance to UV and weather, effect on non-stick and release properties, increase in rub resistance, improved corrosion resistance, thermal stability, insulating properties, and lack of moisture absorption. Figure 2.50 shows SEM micrographs of two grades of free-flowing powder (Polymist F5 and XPH-284) and one grade of micronized powder

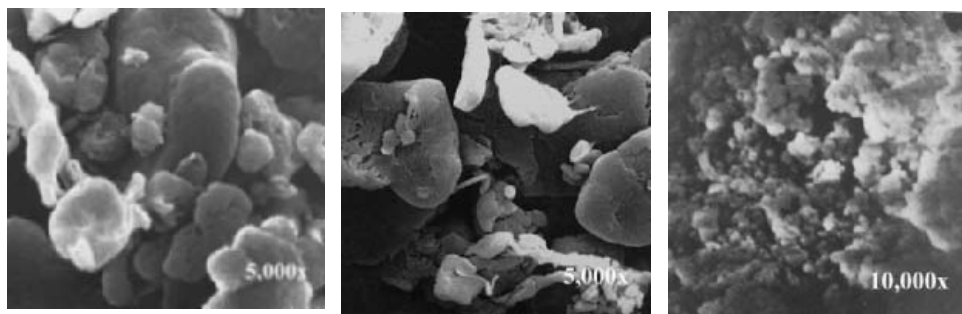


Figure 2.50. SEM micrographs of PTFE powders. Left - Polymist F5 (5000x), center - Polymist XPH-284 (5000x), right - Algoflon L203 (10,000x). *Courtesy of Ausimont USA, Inc., Montedison Group, Thorofare, NJ, USA.*

(Algoflon L203). The micronized grade forms agglomerates of small particles whereas the free-flowing powder is composed of individual particles. Particles have no sharp edges and XPH-284 contains some elongated particles.

Composite Particles, Inc. developed two methods of surface modification of polymeric materials which are used for materials of different shapes and compositions. Here, only the spherical, non-rubber particles are discussed. Further information is included in the section on rubber particles below. One method of surface modification is based on exposing the polymeric powder to a chemically reactive gas atmosphere which oxidizes surface groups to form OH and COOH functionalities. These functionalities are then available for reaction with the components of the matrix into which modified particles are introduced. Vistamer HD and UH are manufactured by this method from polyethylenes of different molecular weights. Two factors can be regulated here: the properties of the core particle and the type and density of functional groups on the surface of these particles. Polyethylene is a material, which without this modification, will not be compatible with most systems. The surface modification allows the incorporation of the material into resins. This improves abrasion resistance, tear strength, and moisture barrier properties and reduces the friction coefficient.

The second method of surface modification permits the formation of a composite particle, the core of which is composed of polymer (UHMWPE or polyimide) and the surface of which is coated with titanium carbide which is hard and abrasion resistant. The composite particles can be incorporated into any suitable matrix resulting in improved abrasion resistance, lowered friction, higher compressive strength, improved creep resistance, etc. This new product is a unique form of raw material which has the potential to improve the properties of many products.

2.1.47 PUMICE

Name: pumice		
Chemical composition: SiO ₂ - 70.9-74.2%, Al ₂ O ₃ - 12.5-13.5%, Fe ₂ O ₃ - 1.5-2%, CaO - 0.7-1.5%, MgO - 0.2-0.5%, Na ₂ O - 3.2-4%, K ₂ O - 3.8-4.5%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.3	Mohs hardness: 5.5	Loss on ignition, %: 3
CHEMICAL PROPERTIES		
Moisture content, %: 2	Adsorbed moisture, %: 140	
OPTICAL PROPERTIES		
Color: off-white, gray		
MORPHOLOGY		
Sieve analysis: 325 mesh residue - 16-22		Specific surface area, m ² /g: 0.4-0.6
MANUFACTURERS & BRAND NAMES: Charles B. Chrystal Co., Inc., New York, NY, USA Chrystal Domestic Pumice - 12 grades differing in particle size Lipari Pumice - high quality Italian pumice Peerless Pumice - the highest quality and uniformity for a broad range of applications		
MAJOR PRODUCT APPLICATIONS: paints (non-skid coatings, textured paints, flatting), chemical carrier, cleaning and polishing liquids, soaps, tooth polishing pastes and powders, cleaning electronic circuit boards		

2.1.48 PYROPHYLLITE

Names: pyrophyllite, aluminum silicate hydroxide		
Chemical formula: AlSi ₂ O ₅ OH		Functionality: OH
Chemical composition: SiO ₂ - 68-75%, Al ₂ O ₃ - 18-25%, Fe ₂ O ₃ - 0.5-0.7%, TiO ₂ - 0.4%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.65 - 2.85	Mohs hardness: 1 - 2.5	
CHEMICAL PROPERTIES		
Moisture content, %: 1		
OPTICAL PROPERTIES		
Refractive index: 1.57	Brightness: 66-78	
Color: white, gray, cream, tan		
MORPHOLOGY		
Crystal structure: monoclinic		Cleavage: one direction
Sieve analysis: 325 mesh sieve residue - 8.8%, 200 mesh - 1-3%		
MANUFACTURERS & BRAND NAMES: Charles B Chrystal Co., Inc., New York, NY, USA Pyrophyllite R-200-C No-Metals, Inc., Affiliate of The China National Non-Metallic Minerals Group, Tucson, AZ, USA Pyrophyllite R.T. Vanderbilt Company, Inc., Norwalk, CT, USA Pyrax A, B, WA		
MAJOR PRODUCT APPLICATIONS: paper, rubber, paints, cosmetics		

2.1.49 RUBBER PARTICLES³⁸²⁻³⁹⁶

Names: rubber particles, rubber filler, ground rubber	
PHYSICAL PROPERTIES	
Density, g/cm³: 1.10-1.15	Coefficient of friction: 1.1
CHEMICAL PROPERTIES	
Moisture content, %: 1	
MORPHOLOGY	
Particle size, μm: 75-2000	
MANUFACTURERS & BRAND NAMES: Composite Particles, Inc., Allentown, PA, USA Vistamer R 4010, 4030, 4040, 4060, 4100, 4200 - surface activated ground rubber. Grades differ in particle size Vistamer RW 4101, 4014, 4020, 4030, 4040, 4060 - surface activated, cryogenically ground rubber. Grades differ in particle size	
MAJOR PRODUCT APPLICATIONS: carpet underlay, shoe soles, roof sealant, roller, wheelchair tire, industrial coating, construction panel, industrial enclosures, foam boot-insert, automotive components, marine equipment, slip-resistant coatings, deck coatings, flexible mold, in-line skate wheels	
MAJOR POLYMER APPLICATIONS: polyurethane, NBR, EVA, PSF, phenoxy, acrylics, epoxy	

The process developed by Composite Particles, Inc. modifies the surface of ground rubber particles. The modification introduces functional groups such as OH, and COOH which can interact with matrix to form hydrogen and covalent bonding. Numerous research papers presented in this book show that functionalization of the filler is the correct approach to improve the performance of filled materials. If untreated ground rubber is introduced into a polymer matrix the results are usually disappointing. There are two reasons: rubber particles have more affinity to themselves than to the surrounding polymer matrix and this hampers the dispersion which is crucial to the properties. Secondly, rubber particles are defect-causing inclusions, usually of substantial dimensions, which reduce mechanical performance. The situation can be reversed by surface modification of the rubber particles to promote a chemical interaction between filler and matrix. The results reported indicate that there is an improved dispersion of particles, in many matrices including water-based materials. Depending on the matrix, various mechanical properties improved, most notably, tear strength and tensile properties. The coefficient of friction of many materials can be increased by the addition of the surface treated rubber filler, Vistamer, to approach values typical of rubber. The modification method is reported to reduce the odor of ground rubber.

2.1.50 SEPIOLITE³⁹⁷⁻³⁹⁸

Names: sepiolite, hydrated magnesium silicate		
Chemical formula: Mg ₄ Si ₆ O ₁₅ (OH) ₂ ·6H ₂ O or Si ₁₂ Mg ₈ O ₃₀ (OH) ₄ (H ₂ O) ₄ ·8H ₂ O		Functionality: OH
Chemical composition: SiO ₂ - 56.1%, MgO - 24.9%, Al ₂ O ₃ - 0.7%, CaO - 1.7%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2-2.3	Mohs hardness: 2-2.5	Melting point, °C: 1550
Loss on ignition, %: 15		
CHEMICAL PROPERTIES		
Moisture content, %: 8-16	pH of water suspension: 7.5-8.5	
OPTICAL PROPERTIES		
Color: white, cream, gray, brown		
MORPHOLOGY		
Particle size, μm: 5-7	Crystal structure: orthorhombic	Micropore volume, cm ³ /g: 9.4
Sieve analysis: 200 mesh sieve residue - 8%		Specific surface area, m ² /g: 240-310
MANUFACTURERS & BRAND NAMES: Non-Metals, Inc. Affiliate of The China National Non-Metallic Minerals Group, Tucson, AZ, USA LH-I, LH-II, LH-III - grades having different sepiolite content		
MAJOR PRODUCT APPLICATIONS: purification agent, asbestos replacement, filler in plastics and rubber, adhesives, blend compatibilizer		
MAJOR POLYMER APPLICATIONS: polyurethane, PS, PVF ₂ , PMMA		

The fibrous structure of sepiolite is composed of talc-like ribbons with two sheets of tetrahedral silica units linked by oxygen atoms to a central octahedral sheet of magnesium. It has needle-shaped particles with channels oriented along the fibers which can absorb liquids. Sepiolite has three kinds of water: hygroscopic water, crystallization water, and constitution water. The crystallization water is removed at 500°C and constitution water is removed at 850°C at which point physical properties change brought about by crystal folding of sepiolite.³⁹⁷

2.1.51 SILICA³⁹⁹⁻⁴¹⁹

About a third of all minerals belong to the silicates class, which is divided into five subclasses. Thirty-five other elements participate in the formation of various silicates which form about 95% of the rocky crust of the earth. Most of these (72%) belong to the subclass of tectosilicates called framework silicates. Feldspar and quartz are the most prominent species in this group.

In filler applications, the silicates group of greatest interest is in the subclass of tectosilicates. Four minerals (quartz, tridymite, cristobalite, and opal) belong to the silica group and three of them (quartz, cristobalite, and opal) are used as fillers or materials for their production.

The composition of pure quartz is close to 100% pure SiO_2 because the structure of the mineral is so compact and perfect that there is no room for silica replacement by any other element. Also, quartz is insoluble in all acids except HF, which further contributes to its purity. Quartz forms many micro- and cryptocrystalline varieties. Some of them are well-known as semiprecious stones (amethyst, citrine, agate, tiger-eye, etc.).

Unlike quartz, cristobalite has an open structure, allowing some fraction of silicon (2-3%) to be replaced by other elements, such as, Al, Na, or Ca. Still, 95% of the mineral is formed by SiO_2 . The natural cristobalite does not exist in concentrations that make mining feasible therefore it is produced by synthesis (see separate section on cristobalite). Both minerals are found in volcanic rocks, but quartz, which constitutes 12.5% of the Earth's crust, is found everywhere, since it does not change or erode. Sandstone is one of the sources of quartz.

It should be mentioned here that diatomite or diatomaceous earth, formed from an accumulation of siliceous material of diatoms, is classified as an opal. This mineral is discussed under its commonly accepted name – diatomaceous earth – in the separate section above.

The common availability of silica is not the sole reason for its extensive use. Probably, it is the chemical inertness and durability of silica which determined its popularity. The fillers discussed here include not only natural minerals but also a variety of synthetic products. Natural products can be divided into crystalline and amorphous. Crystalline silica fillers include sands, ground silica (or silica flour), and a form of quartz – tripoli, whereas the amorphous types include diatomaceous earth.

In addition to the natural products, synthetic materials are in common use. Two methods of production are used: pyrogenic or thermal (commonly known as fumed silica grades) and wet process (commonly known as precipitated silica).

This mixture of natural and synthetic materials was taken as a base for creation of the groups below, which are grouped by their common name rather than by their origin.

2.1.51.1 FUMED SILICA⁴²⁰⁻⁴²⁹

Names: fumed silica, pyrogenic silica, thermal silica		CAS #: 112945-52-5 for treated differs
Chemical formula: SiO ₂	Functionality: OH or modification-dependent	
Chemical composition: SiO ₂ - 96-99.8%, Al ₂ O ₃ - 0.05-1.3%, Fe ₂ O ₃ - 0.003-0.06%, TiO ₂ - 0.03%		
Trace elements: Al, As, Au, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, In, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Sc, Sn, Th, U, Zn. The trace elements content is below the limits specified by the requirements of major pharmacopoeias		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2-2.2	Decomposition temp., °C: >2000	
Loss on ignition, %: 1-2.5 (hydrophilic), 1-7 (hydrophobic)		
Thermal conductivity, W/K · m: 0.015	Maximum temperature of use, °C: 850	
CHEMICAL PROPERTIES		
Chemical resistance: non-reactive with acids with the exception of HF, unstable in alkalis		
Moisture content, %: 0.5-2.5 (hydrophilic) 0.5 (hydrophobic)	Adsorbed moisture, %: 6	
pH of water suspension: 3.6-4.5 (hydrophilic), 3.5-11 (hydrophobic)	Water solubility, %: 0.015	
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 1.46	Volume resistivity, Ω-cm: 10 ¹³	
MORPHOLOGY		
Particle shape: spherical	Crystal structure: amorphous	Porosity: non porous
Particle size primary, nm: 5-40	Oil absorption, g/100 g: 100-330	Appearance: fluffy white powder
Density of silanol groups, 1/nm ² : 1.5-4.5		Aggregate size, μm: 0.2-15
Sieve analysis: 325 mesh sieve residue - 0.05-1%	Specific surface area, m ² /g: 50-400	
MANUFACTURERS & BRAND NAMES:		
Cabot Corporation, Cab-O-Sil Division, Tuscola, IL, USA Cab-O-Sil L-90, LM-130, LM-150, M-5, MS-55, H-5, HS-5, EH-5 - hydrophilic grades of fumed silica differing in average primary particle size and BET surface area Cab-O-Sil TS-720, TS-610, TS-530, TS-500 - hydrophobic grades differing in particle size and BET surface area and treatment chemistry Cab-O-Sil LM-150D, M-7D, M-75D - densified grades		
Degussa AG, Frankfurt/Main, Germany Aerosil 90, 130, 150, 200, 300, 380, OX50, TT600, MOX80, MOX170 - hydrophilic grades of fumed silica differing in average primary particle size and BET surface area Aerosil COK 84 - mixture of Aerosil and highly dispersed Al ₂ O ₃ in ratio of 5:1 for thickening of aqueous systems Aerosil R202, R805, R812, R812S, R972, R974, R104, R106, R504, R816 - hydrophobic grades differing in particle size and BET surface area and treatment chemistry Aerosil K315, K328, K330, K342, DCF784, SATESSA28, SATESSA42 - 30% dispersions		
Harwick Standard Distribution Corporation, Akron, OH, USA Silica S - low cost pyrogenic silica filler for rubber		
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MANUFACTURERS & BRAND NAMES:

Wacker-Chemie GmbH, München, Germany

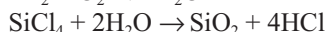
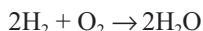
HDK S13, V15, N20, T30, T40 - hydrophilic grades of fumed silica differing in average primary particle size and BET surface area

HDK H15, H20, H30, H2000, H2000/4, H3004, H2015EP, H2050EP - hydrophobic grades differing in particle size, BET surface area, and treatment chemistry

MAJOR PRODUCT APPLICATIONS: paints, coatings, primers, powder coatings, printing inks, pigments, diazo paper, toothpaste, tablets, powders, aerosols, ointments, creams, dry toner, sealants, rubber goods, adhesives, cable and wire, laminates, gel coats, body putties, defoamers, food, insecticides, lubricants, animal feeds, fertilizers, polishes, reproduction papers, waxes

MAJOR POLYMER APPLICATIONS: polyurethane, epoxy, silicone, polychloroprene, PSF, acrylics, PVC, polyesters, alkyd, fluoroelastomers, NR, SBR

The product obtained from the vapor process is frequently termed fumed silica because it looks like smoke or fumes. This process was developed by applying carbon black production technology and equipment to silica tetrachloride in an invention by Degussa AG. Fumed silica manufactured is presently based on Degussa's license, which was sold to only a few other corporations. Metallic silicon and gaseous dry HCl are reacted to form silica tetrachloride, which is mixed with hydrogen and air and fed into the burner tube of the reactor where the following reactions occur:



The reaction temperature is around 1800°C. The HCl formed in the process is recycled. The primary particles of silica leaving the burner are in a molten state; therefore, on collision they are able to coalesce, forming bigger particles. When particles proceed through the reactor, they cool down, and around 1710°C they become solid and are no longer able to recombine. Before this happens, primary particles fuse with one another and form chain-like, branched aggregates. The size of primary grains is usually in the range of 7 to 30 nm, which produces a specific surface area in the final product from 400 to 100 m²/g. Below the melting point of silica (1710°C) particles still collide and form aggregates due to mechanical entanglement or agglomeration. Agglomeration also occurs in the collection process. These mechano-physical aggregates can be disintegrated on mixing during the processing of material formulated with fumed silica. Some trace amounts of HCl (less than 200 ppm) are retained in the product. The process of production of fumed silica sometimes includes compacting, which increases the product density by 2-2.5 times. The manufacturing process can be easily regulated with respect to primary particle size and the size and structure of the aggregate. Figure 2.51 shows the schematic diagram of production process.

Figure 2.52 illustrates the difference between fumed silica and crystalline silica. The diagram for fumed silica does not show absorption peaks whereas the diagram for quartz, which is a crystalline product, does. The amorphous nature of

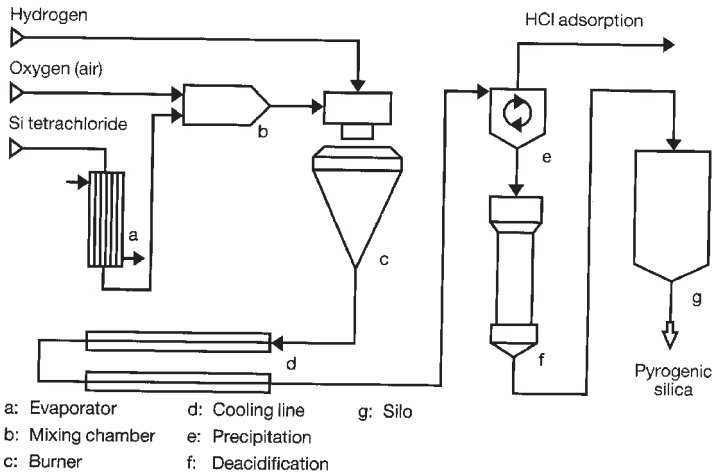


Figure 2.51. Production of Aerosil. *Courtesy of Degussa AG, Frankfurt/Main, Germany.*

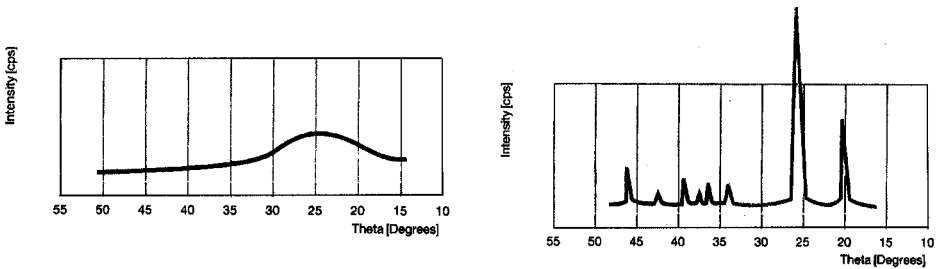


Figure 2.52. X-ray diagram of fumed silica (left) and quartz (right). *Courtesy of Wacker-Chemie GmbH, München, Germany.*

fumed silica is probably caused by the fast cooling process, which takes a few thousandths of a second. This permits the classification of fumed silica as amorphous and is an important benefit for those working with fumed silica that, unlike the crystalline forms of silica, it does not cause silicosis.

Figure 2.53 explains differences between the chemical composition of surfaces of hydrophilic, and silane treated, hydrophobic, fumed silica. The isolated hydroxyl groups and hydrogen-bonded hydroxyl groups are both hydrophilic, whereas the siloxane group is hydrophobic. These chemical groups make the surface of untreated silica hydrophilic and are essential for its properties and applications. Chemical and thermogravimetric analysis indicate that there are approximately 3 to 4.5 hydroxyl groups per square nm of silica surface. On the surface of hydrophobic fumed silica, dimethylsilyl, trimethylsilyl,

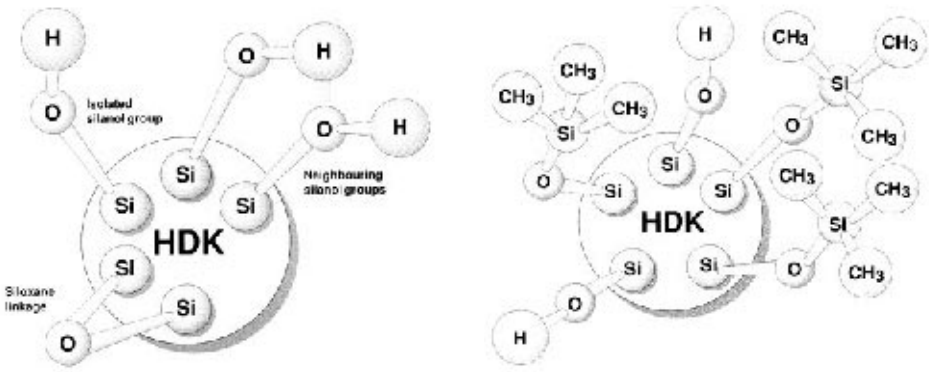


Figure 2.53. Chemical structure of untreated (left) and treated (right) fumed silica surface. *Courtesy of Wacker-Chemie GmbH, München, Germany.*

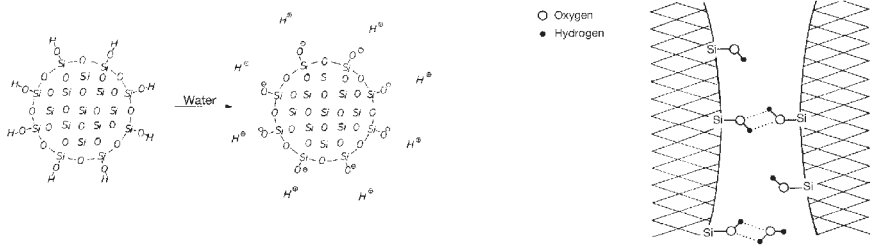


Figure 2.54. The origin of acidic properties of fumed silica (left) and the mechanism of hydrogen bonding (right). *Courtesy of Degussa AG, Frankfurt/Main, Germany.*

dimethylsiloxane, and octyl groups replace some hydroxyl groups. Typically about 1.5 OH groups per square nm remain after treatment. The extent of replacement regulates the hydrophobic properties of fumed silica.

Fumed silica is a weak acid and hydroxyl groups are essential in hydrogen bonding (Figure 2.54).

The mechanism of thickening of liquids by fumed silica is explained by hydrogen bond formation between neighboring aggregates of silica, leading to the formation of a regular network. On the application of shear some of these bonds are broken which reduces viscosity. The initial state is regained when material is left to stand. Hydroxyl groups, needed for this process, are converted to siloxane groups on heating to 110°C, which retards the reaction. Fumed silica, on leaving the factory, has 0.5-2.5% moisture, which is partially needed for the thickening process but, at the same time what water remains is reactive to some of the components in

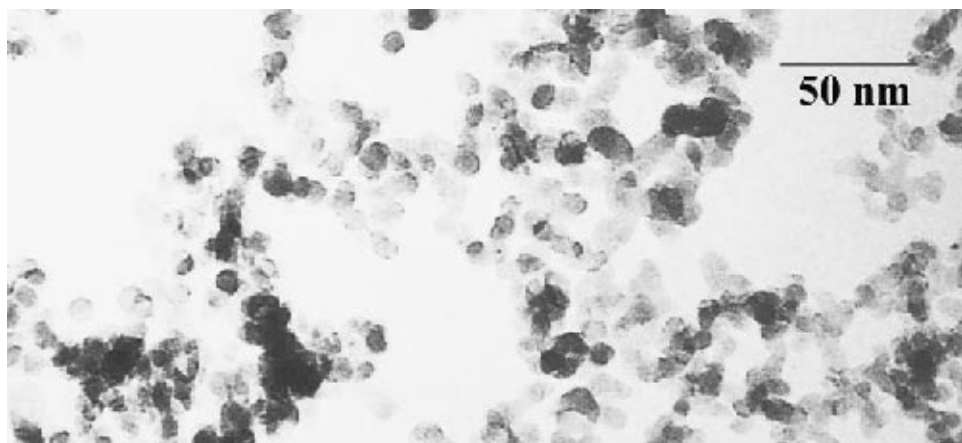


Figure 2.55. SEM micrograph of Wacker HDK N20. Magnification 300,000x. *Courtesy of Wacker-Chemie GmbH, München, Germany.*

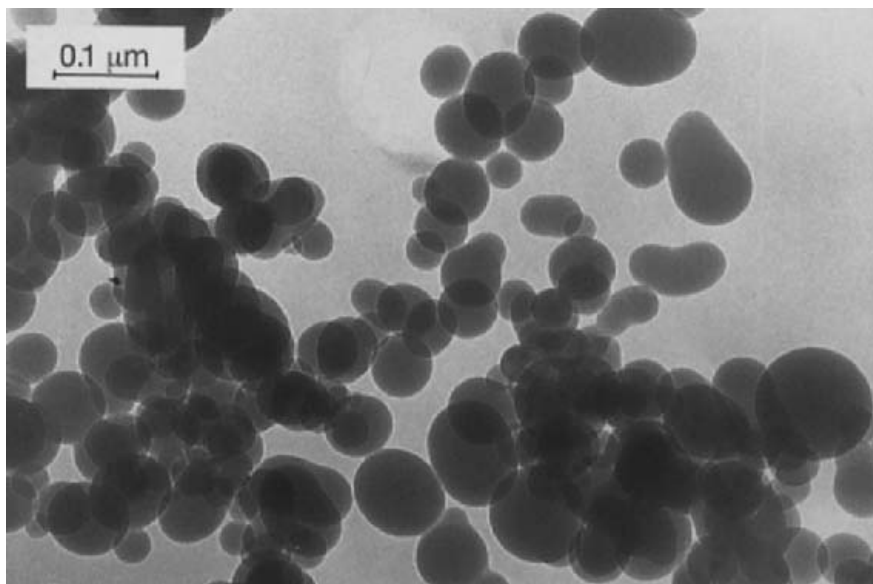


Figure 2.56. TEM micrograph of Aerosil OX50. *Courtesy of Degussa AG, Frankfurt/Main, Germany.*

industrial formulations, such as with ketimines used for polyurethane prepolymer curing.

Figure 2.55 shows the morphology of fumed silica which is composed of grain-like agglomerates. Figure 2.56 shows that particles are spherical. The morphology of primary particles is easier to observe in Aerosil OX50 which has a larger size of primary particles (40 nm) and TEM display information on the shape of particle in a two dimensional scale. A primary particle of fumed silica is built up of about 10,000 SiO_2 units.

The mixing process of fumed silica must be carefully designed to control the degree of thickening. Fumed silica particles are composed of aggregates and agglomerates which are dispersed to form smaller aggregates. Overmixing reduces the size of aggregates too much and aggregates cannot form network of chains interconnected throughout the mixture. Instead, they will form only a partial network. Such overmixing is irreversible process.

In industrial products, the use of fumed silica will confer thixotropy, sag resistance, particle suspension, emulsifiability, reinforcement, gloss reduction, flow enhancement of powders, anti-caking, anti-slip, anti-blocking, etc. Because of its effect on these important properties, fumed silica is widely used in many industries.

2.1.51.2 FUSED SILICA

Name: fused silica		CAS #: 60676-86-0
Chemical formula: SiO ₂		Functionality: none or from silane
Chemical composition: SiO ₂ - 98.5-99%, Al ₂ O ₃ - 0.25-1%, Fe ₂ O ₃ - 0.05%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.2	Mohs hardness: 7	Loss on ignition, %: 0.1-0.45
Thermal conductivity, W/K · m: 1.1	Linear coefficient of thermal expansion, 1/K: 0.5x10 ⁻⁶	
CHEMICAL PROPERTIES		
Chemical resistance: resistant to acids		Moisture content, %: 0.1
pH of water suspension: 9		
OPTICAL & ELECTRICAL PROPERTIES		
Color: white	Dielectric constant: 3.78	Loss tangent: <1x10 ⁻³
Specific electric conductivity, S/cm: 10 ⁻¹⁷ -10 ⁻¹⁸		
MORPHOLOGY		
Particle size, μm: 4-28	Oil absorption, g/100 g: 17-27	
Specific surface area, m ² /g: 0.8-3.5		
MANUFACTURERS & BRAND NAMES: Denki Kagaku Kogyo Co., Ltd., Ibaraki, Japan FB-30, FB-35, FB-48, FB-74 - spherical fused amorphous silica Quarzwerke GmbH, Frechen, Germany Silbond FW61, FW12, FW100, FW300, FW600 - fused silica flours of different particle sizes. Available with aminosilane (AST grade) and epoxysilane (EST)		
MAJOR PRODUCT APPLICATIONS: encapsulating material for integrated circuits, electric components, conductors		
MAJOR POLYMER APPLICATIONS: epoxy, PPS		

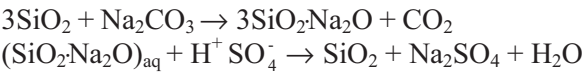
Fused silica flour is produced from electrically fused SiO₂ by iron free grinding followed by air separation. As an option, it may be coated with silane. Quarzwerke GmbH treats flour with amino and epoxysilanes. Denki Kagaku Kogyo Co., Ltd. manufactures spherical grades of fused amorphous silica.

The properties of this filler can be appreciated when compared with silica sand discussed below in separate section. The comparison shows a very low linear thermal expansion coefficient, thermal conductivity, and very high specific electrical conductivity. These unusual properties, similar to those of the pure quartz crystal, are exploited in applications in electronics.

2.1.51.3 PRECIPITATED SILICA^{429,432-440}

Name: precipitated silica		CAS #: 63231-67-4
Chemical formula: SiO ₂		Functionality: OH or from silane
Chemical composition: SiO ₂ - 97.5-99.4%, Fe ₂ O ₃ - 0.01-0.1%, Al ₂ O ₃ - 0.6%, TiO ₂ - 0.07%, CaO - 0.5%, MgO - 0.2%, Na ₂ SO ₄ - 0.8-1.5%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 1.9-2.1	Mohs hardness: 1	Loss on ignition, %: 3-18
CHEMICAL PROPERTIES		
Moisture content, %: 3-7	Adsorbed moisture, %: 7-20	OH group density, 1/nm ² : 5-12
pH of water suspension: 3.5-9		
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 1.46	Dielectric constant: 1.9-2.8	Loss tangent: 0.00001-0.02
Color: white	Volume resistivity, Ω-cm: 5.7x10 ¹¹ -4.5x10 ¹⁴	
MORPHOLOGY		
Predominant pore diameter, nm: 30		Hegman fineness: 5-7
Agglomerate size, μm: 1-40	Oil absorption, g/100 g: 60-320	Primary particle size, nm: 5-100
Sieve analysis: 325 mesh sieve residue - 0.002-0.2%		Specific surface area, m ² /g: 12-800
MANUFACTURERS & BRAND NAMES: Charles B. Chrystal Co., Inc., New York, NY, USA Precipitated Silica # 32, #22 - flatting agents, food and pharmaceutical grades Degussa AG, Frankfurt/Main, Germany Ultrasil VN 3, FK 160 FK 300 DS, FK 310 - hydrophilic Sipernat D 10, D 17 - hydrophobic PPG Industries, Pittsburgh, PA, USA Lo-Vel 27, 275, 28, 29, 39, 66, HSF, Inhibisil - flatting agents Hi-Sil T-600, T-700 - thickeners Rhône Poulenc, Paris, France Zeosil Z91, Z93, Z162, Z172A, Z172B, 175 MP		
MAJOR PRODUCT APPLICATIONS: tires, sealants, adhesives, coatings, paints, topcoat lacquers, coil coating, micro texture finish, wood finishes, thixotropes, office furniture		
MAJOR POLYMER APPLICATIONS: nitrocellulose, melamine, polyester, acrylics, silicone, alkyd, epoxy, PVC, EPDM, NR, SBR		

Precipitated silica is produced from sodium silicate through its reaction with sulfuric and hydrochloric acids. The following reactions apply:



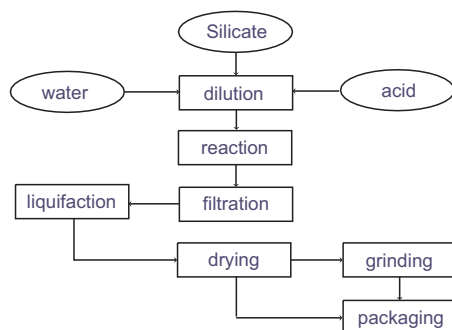


Figure 2.57. Precipitated silica process. After Bomo F, Meeting of the Rubber Division, ACS, Montreal, May 5-8, 1996, paper E.

From these reactions it is quite evident that the concentration of the remaining Na_2SO_4 is one of the quality factors. Figure 2.57 shows the schematic diagram of the process.

Concentration of reactants, rates of addition, fraction of theoretical silicate in the reaction, and temperature are the process variables determining the properties of the final product, such as, oil number, specific surface area, porosity, primary particle and agglomerate size and shape, brightness, density, and hardness. After the reaction is complete, the product is separated by filtration, washed, dried, and milled. Final products are sometimes indexed in a manner similar to carbon blacks, which distinguishes the following grades: very high structure (VHS), high structure (HS), medium structure (MS), low structure (LS), and very low structure (VLS).

Moisture concentration in the final product is comparably high (3-7%) and three types of water are available: free water, which can be removed at 105°C ; adsorbed water (hydrogen bonded water), which is removed on heating from 105 to 200°C ; and constitutional water, which can only be removed in a temperature range from 700 to 900°C . The mechanism of thickening is similar to that of fumed silica and involves bridging between two particles by formation of hydrogen bonding formed by the interaction of silanol and siloxane groups. Precipitated silica has more silanol groups than fumed silica. The product has a lower concentration of silica since it usually contains an admixture of sodium sulfate (approximately up to 1.5%).

Recent advances in the application of precipitated silica in tires will rapidly increase consumption of this filler beyond that which it enjoys in its traditional markets. Regulation of thixotropic properties of industrial products and the flattening of coatings and paints are important applications for these fillers. Figure 2.58 shows the mechanism of flattening. Very good dispersion of precipitated silica facilitates uniform distribution of its agglomerates. The presence of agglomerates close to surface causes surface roughening.

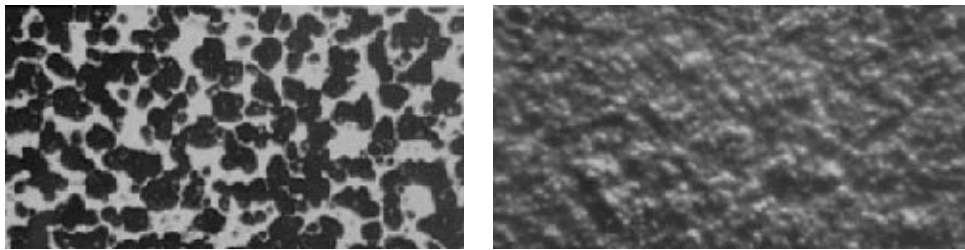


Figure 2.58. Surface flatting mechanism by precipitated silica, Lo-Vel HSF. Left - distribution of agglomerates, right - surface roughness of coating. *Courtesy of PPG Industries, Inc., Pittsburgh, PA, USA.*

2.1.51.4 QUARTZ (TRIPOLI)

Names: microcrystalline silica powder, tripoli, novaculite, quartz silica		CAS #: 14808-60-7
Chemical formula: SiO ₂		Functionality: none or silane modified
Chemical composition: SiO ₂ - 99.1-99.4%, Fe ₂ O ₃ - 0.04%, Al ₂ O ₃ - 0.1%, TiO ₂ - 0.02%, CaO - 0.01%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.65	Mohs hardness: 7	Loss on ignition, %: 0.2
Maximum temperature of use, °C: 573		Specific heat, kJ/kg · K: 0.8
CHEMICAL PROPERTIES		
Moisture content, %: 0	Adsorbed moisture, %: 8.7	pH of water suspension: 6-7.8
OPTICAL PROPERTIES		
Refractive index: 1.55	Color: white	Brightness: 80
MORPHOLOGY		
Particle shape: platy	Crystal structure: trigonal	Hegman fineness: 0-7
Particle size, μm: 2-19	Oil absorption, g/100 g: 17-20	
Sieve analysis: 325 mesh sieve residue - 0.1-1%		
MANUFACTURER & BRAND NAMES: Charles B. Chrystal Co., Inc., New York, NY, USA Silica 3-37 - micronized platy silica Malvern Minerals Company, Hot Springs National Park, AR, USA Novacite 200, 325, 1250, Daper, L-207A, L-337 - grades having different particle size but with the same oil absorption Novakup - silane treated Novacite grades		
MAJOR PRODUCT APPLICATIONS: paints, coatings, corrosion-resistant finishes, casting and potting compounds, powder coatings, grouts, molding articles, electrostatic coatings, pipe linings, silicon rubber articles, abrasive materials		
MAJOR POLYMER APPLICATIONS: polyurethanes, alkyd, acrylics, silicon PVC		

The range of materials are produced by Malvern Minerals Company from the high purity mineral – Novaculite - found in Hot Springs, Arkansas. The platy disc shaped particles have many properties important to industrial applications. Novacite has low oil absorption and water sorption, good flattening effect, chemical inertness, and it gives a chalk-free, UV-resistant and non-staining coatings with typical paint binders. Figure 2.59 shows morphological structure of this unique material. The platelet particles combine to form clusters.

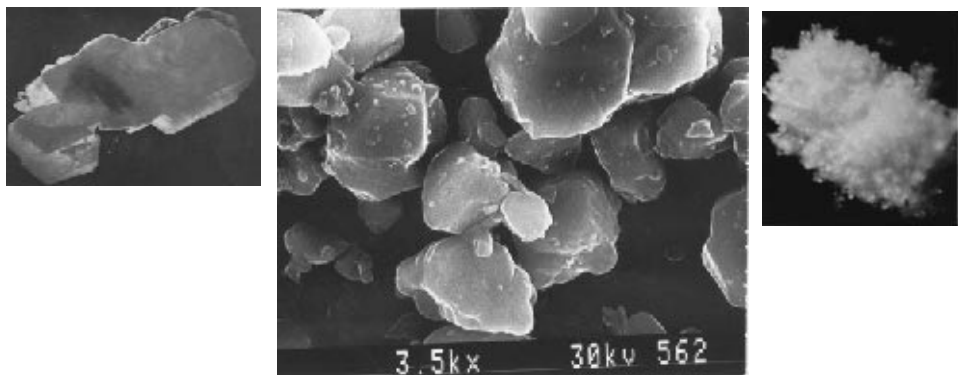


Figure 2.59. Novacite morphology. Left - single platelet, middle - distribution of sizes, right - cluster. *Courtesy of Malvern Minerals Company, Hot Springs National Park, AR, USA (micrographs of platelet and cluster).*

2.1.51.5 SAND⁴⁴¹⁻⁴⁴⁴

Names: sand, silica flour, ground silica		CAS #: 14808-60-7
Chemical formula: SiO ₂		Functionality: none or from silane
Chemical composition: SiO ₂ - 97.5-99.8%, Al ₂ O ₃ - 0.05-2%, Fe ₂ O ₃ - 0.02-0.05%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.65	Mohs hardness: 7	Loss on ignition, %: 0.1-0.55
Thermal conductivity, W/K · m: 7.2-13.6	Linear thermal expansion coefficient, 1/K: 14x10 ⁻⁶	
CHEMICAL PROPERTIES		
Moisture content, %: 0.1	pH of water suspension: 6.8-7.2, 7-9 (silane treated)	
OPTICAL & ELECTRICAL PROPERTIES		
Specific electric conductivity, S/cm: 10 ⁻¹⁴ -10 ⁻¹⁶		Brightness: 80-88
Dielectric constant: 4	Reflectance: 82-90	
MORPHOLOGY		
Particle size, µm: 2-90	Oil absorption, g/100 g: 14-28	Hegman fineness: 0-4
Sieve analysis: residue on 325 mesh sieve - 0.1-47%		Specific surface area, m ² /g: 0.3-6
MANUFACTURERS & BRAND NAMES: Charles B Chrystal Co., Inc., New York, USA High Purity Quartz Type 31/90, Type P, Starsil Spherical Silica - natural silica of different sizes and purity Quarzwерke GmbH, Frechen, Germany Millisil W 3, 4, 6, 8, 10, 12 - iron-free grinding of processed silica sand. Particle size decreases with grade number increasing Sikron SF 300, 500, 600, 800, SH 300, 500 - micronized silica flours Silbond W 6, 12, 100, 600, 800 - silica flours treated with various silanes (AST - amino, EST - epoxy, MST - methylacrylo, RST - trimethyl, TST - methyl, VST - vinyl) US Silica Company, Berkeley Springs, WV, USA Full range of quality sands and silica flours under the following brand names Mystic White, F-series Foundry sands, Penn Sand, Q-Mix, Q-Rok, Sil-Co-Sil, Supersil, Min-U-Sil		
MAJOR PRODUCT APPLICATIONS: high temperature synthesis of wollastonite, synthesis of calcium hydro silicates, sealants, stucco, primers, road marking formulations, resin casting, adhesives, mortars, coatings, paint, lacquers, special papers, construction elements, pin insulators, machine tools, lining for chemical pumps		
MAJOR POLYMER APPLICATIONS: epoxy, polyurethanes, polyesters, PMMA, PVC, PE		

The production of sand fillers is simple because it includes, at most, only washing and classification into grades differing in grain size. Because sand has a negligible degree of porosity it has an extremely low specific surface area in the range from 40 to 160 cm²/g. The material usually contains more than 99.7% SiO₂, with absorbed water being at a negligible level (0.1%). Ground silica sand is produced in a similar manner, except that pulverizing is included. Ground silica can easily be distinguished under the microscope because it has irregular grains. Grinding considerably increases the surface area into the range from 1000 to 5000 cm²/g, with an

average particle size in a range from 16 to 4 μm . High quality grades are produced by grinding sand in iron-free ball mills followed by classification controlled by a laser technique with Cilas-granulometers. Material from this process is stored in moisture-free silo. Figure 2.60 shows the morphology of silica sand.

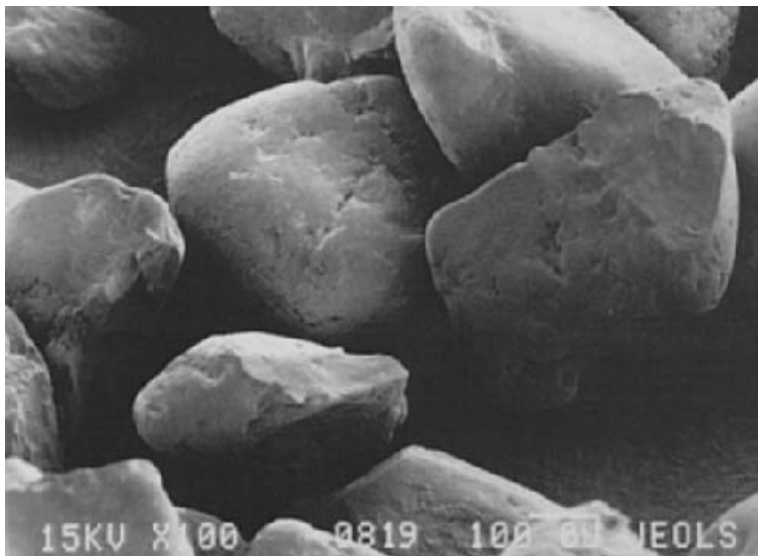


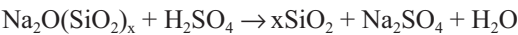
Figure 2.60. Silica sand (100x). *Courtesy of Quarzwerke GmbH, Frechen, Germany.*

The content of iron is one of important indicators of quality of silica flour for various applications, especially for external coatings. The presence of iron causes formation of rusty streaks which form when the iron oxidizes. The good quality material for these applications should have a Fe_2O_3 content below 0.03%.

2.1.51.6 SILICA GEL⁴⁴⁵⁻⁴⁴⁷

Names: silica gel, amorphous silica		CAS #: 7699-41-4
Chemical formula: SiO ₂		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.2-2.6	Mohs hardness: 6	
CHEMICAL PROPERTIES		
pH of water suspension: 6.5-7.5		
MORPHOLOGY		
Particle size, μm: 2-15	Oil absorption, g/100 g: 80-280	Pore radius, nm: 5-40
Specific surface area, m ² /g: 40-850		
MANUFACTURERS & BRAND NAMES: Crosfield Group, Warrington, UK Gasil 200 DF, Gasil HP 370 Macherey Nagel Nucleosil Nu 100-30, 1000-30		
MAJOR PRODUCT APPLICATIONS: paints, coatings, drying of materials, putties, window spacers		
MAJOR POLYMER APPLICATIONS: alkyd, polyurethanes		

Silica gel is produced according to the following reaction:



The product of reaction contains about 75% water and is subjected to a drying process. Drying takes place in a rotary kiln followed by milling of the material which has been previously washed with hot alkaline water (which reinforces the matrix, decreases shrinkage, and produces larger pores), results in the xerogels. Super-critical drying or replacing water by methanol, before drying, decreases the crushing force and produces aerogels which have up to 94% air space. The average particle size is in a range from 2 to 15 μm. Further changes in the particle size can be accomplished by milling and air classification. The specific surface area is very high due to the high porosity (40-850 m²/g). Hydrogels have a pore radius (7-12 nm) similar to xerogels (5-15 nm), while aerogels have a higher pore radius (10-40 nm). Small particles and high porosity result in high oil absorption, in a range from 80 to 280%.

Silica gels of specific pore size (e.g., Gasil grades) are becoming important in surface matting of paints.

2.1.52 SILVER POWDER AND FLAKES⁴⁴⁸

Names: silver powder, silver flakes, atomized silver powder, silver/palladium powder and flakes		CAS #: 7440-22-4
Chemical formula: Ag		Functionality: none
Chemical composition: Ag - 99.3-99.9%; silver/palladium - all ratios available		
Trace elements: heavy metals - 0.02%, Na+K - 0.01-0.02%		
PHYSICAL PROPERTIES		
Density, g/cm³: 10.5	Mohs hardness: 2.5-4	Melting point, °C: 962
Thermal conductivity, W/K · m: 450	Specific heat, kJ/kg · K: 0.188	
Tensile strength, MPa: 290		
CHEMICAL PROPERTIES		
Chemical resistance: soluble in strong acids		
ELECTRICAL PROPERTIES		
Resistivity, Ω-cm: 1.59x10 ⁻⁶		
MORPHOLOGY		
Particle shape: spherical or flake	Crystal structure: cubic	Particle size, μm: 0.25-25
Sieve analysis: 325 mesh residue - traces		Specific surface area, m²/g: 0.15-6
MANUFACTURER & BRAND NAMES: Technic Inc., Woonsocket, RI, USA Silpowder 171, 172, 173, 222, 223, 225, 228, 251, 252, 253, 263, 271, 335, 336, 995 - chemically precipitated powders of different particle sizes for applications listed below Silsphere 514, 517, 519 - chemically precipitated spherical powders Silflakes 131, 132, 134, 135, 138, 235, 237, 239, 241, 242, 282, 285, 299, 255, 450, 556 - mechanically flatted powders to form flakes, mostly for conductive applications Silver/Palladium powders 600 and 700 Series - chemically co-precipitated spherical powders		
MAJOR PRODUCT APPLICATIONS: conductive inks, pastes, coatings, adhesives, thick films, battery plates, electrical contacts, powder metallurgy, capacitor inks		
MAJOR POLYMER APPLICATIONS: epoxy and others		

Figure 2.61 shows the morphology of powder (product of chemical precipitation) and flakes made by mechanical flattening of powders.

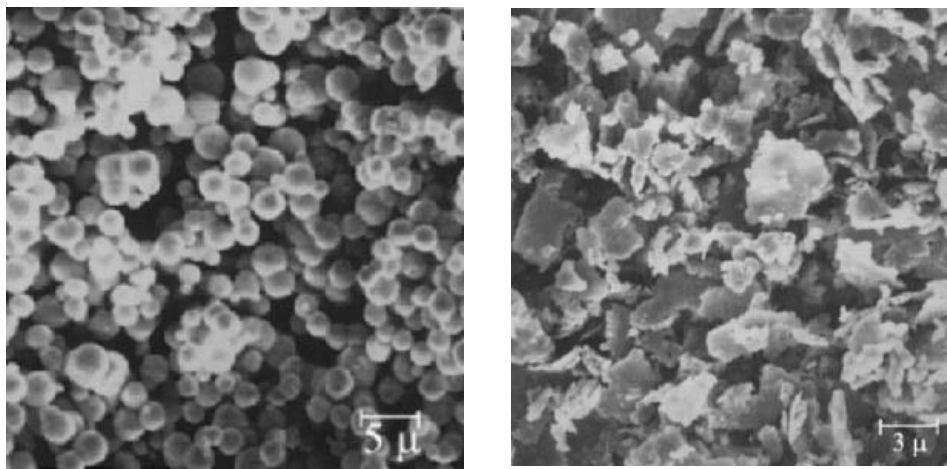


Figure 2.61. Silver powder and flake. *Courtesy of Technic, Inc., Woonsocket, RI, USA.*

2.1.53 SLATE FLOUR

Name: slate flour		CAS #: 1335-30-4
Chemical formula: variable		Functionality: OH
Chemical composition: SiO ₂ - 35-62.3%, Al ₂ O ₃ - 8.5-20.7%, Fe ₂ O ₃ - 2.5-7.65%, CaO - 0.2-2.5%, MgO - 0.4-2%, Na ₂ O - 0.3-1.2%, K ₂ O - 2.2-3.6%, carbon - 28.9-29.7%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.1-2.7		
CHEMICAL PROPERTIES		
Chemical resistance: reacts with acids and alkalis		
Moisture content, %: 1	pH of water suspension: 6.5-8.1	
OPTICAL PROPERTIES		
Color: red, light-dark gray		
MORPHOLOGY		
Sieve analysis: residue on 325 mesh sieve - 1%		Oil absorption, g/100 g: 22-32
MANUFACTURERS & BRAND NAMES: Keystone Filler & Manufacturing Co., Muncy, PA, USA Light Gray Slate Flour, Dark Gray Slate Flour, Red Slate Flour Charles B. Chrystal, Co., Inc., New York, NY, USA Light Gray Slate Flour, Dark Gray Slate Flour		
MAJOR PRODUCT APPLICATIONS: inexpensive filler		

2.1.54 TALC⁴⁴⁹⁻⁴⁷²

Names: talc, magnesium silicate hydroxide, phyllosilicate		CAS #: 14807-96-6
Chemical formula: Mg ₃ Si ₄ O ₁₀ (OH) ₂		Functionality: OH or silane modified
Chemical composition: SiO ₂ - 46.4-63.4%, MgO - 24.3-31.9%, CaO - 0.4-13%, Al ₂ O ₃ - 0.3-0.8%, Fe ₂ O ₃ - 0.1-1.8%		
Trace elements: Pb, As, Cd, Zn, Ba, Sb		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.7 - 2.85	Mohs hardness: 1-1.5	Loss on ignition, %: 4.8-17
Thermal conductivity, W/K · m: 0.02	Maximum temperature of use, °C: 900	
Thermal expansion coefficient, 1/K: 8	Specific heat, kJ/kg · K: 0.82	
CHEMICAL PROPERTIES		
Moisture content, %: 0.1-0.6	pH of water suspension: 8.7-10.6	
Water solubility, %: 0.1		Acid soluble matter, %: 2
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 1.57-1.59	Brightness: 78-93	Whiteness: 70-94
Color: white		Dielectric constant: 7.5
MORPHOLOGY		
Particle shape: platy	Crystal structure: monoclinic	Cleavage: basal
Particle size, μm: 1.4-19	Oil absorption, g/100 g: 22-57	Hegman fineness: 0-7
Aspect ratio: 5-20	Particle thickness, μm: 0.2-6	
Sieve analysis: 325 mesh sieve residue - 0.1-2%		Specific surface area, m ² /g: 2.6-35
MANUFACTURERS & BRAND NAMES: Barretts Minerals, Inc., USA MP12-50, MP44-26 Canadian Talc Ltd. Cantal 45-80 Charles B. Chrystal Co., Inc., New York, NY, USA AGSC - talc from South China, meeting CTFA Specification Purtalc 6030, 428 - USP Grade Talc 523, Delusted, #2 French, #44 - lower price talc Micro Talc, 928, Bacteria-free, Sugarloaf grades, Purtalc, Osmanthus, Vertal CO+ - cosmetic grades Paper Talc, 9610, 7022, 10-MO - industrial grades		

continued on the next page

MANUFACTURERS & BRAND NAMES:

Luzenac Europe, Toulouse, France

Paper grades

Lithicoat P2F, T3F, T4A - grades for matt wood-free art paper which are the mixtures of talc, chlorite and dolomite

Mistron - talc for pitch control

Malusil Naintsch - absorbs interfering anionic substances without impairment of hydrophobic and organophilic character of material due to the activation process which changes its zeta potential

Mistron Vapor C, P2, P5 - microcrystalline talc © - compacted grades with 3% water)

Luzenac 0, 1 - general purpose talc for paper industry

Plastic grades

Luzenac 1445, 20M0, 20M00S, 00S - highly lamellar talc with low abrasiveness from French Pyrenees

Steamic 00S, 00S D - micronized and finely ground talc for PP dashboards and bumpers

1N, Extra 5/0-M10, Prever, M8, M10C, M8C, M30 - talc from Val Germanasca mine in Italy for rubber and plastics

Paint grades

1N-M20, Prever M10, Extra 5/0 - high purity talc from Val Germanasca mine in Italy

Mistrofil 325, 400 - microcrystalline chlorite

Mistron 705, 754, Monomix, Super-20, Monomix-E, PE-60 - microcrystalline talc

Naintsch E, SE, ASE, - extremely lamellar structure and talcs containing dolomite

Luzenac 00C, 20M0, 10M0, Steabright, Steapac - various finishes in decorative and industrial paints

Milwhite, Inc., Houston, TX, USA

TDM crude, 85, 92, 95, 98, 300, 325, W-93, W-98, W-286, W-300, W-325, CS-92 - industrial talcs

Westex 60/40, 65/35, 73/27, 80/20 - blended talcs

Westex FF - calcinated talc

Non-Metals, Inc. Affiliate of The China National Non-Metallic Group, Tucson, AZ, USA

talc - a broad range of grades for various applications from four plants located in different parts of China

Pfizer, USA

Microtalc

Polar Minerals, Mt. Vernon, IN, USA

9100 Series (9102, 9103, 9107, 9110) - plastic additives, free of asbestos and high purity

9200 Series (9202, 9202 D, 9205) - rubber, paper, and coatings applications

9300 Series (9305, 9310) 9400 Series (9410) - polypropylene, paint, coatings, polyester, adhesives

9600 Series (9602, 9603, 9607, 9610) - broad range of applications in plastics, rubber, inks, coatings, adhesives and sealants

9800 Series (9810), 9900 Series (9910) - economical grades

Ultra (2000, 3000, 4000, 5000) - cosmetic grades

Gel, Body medium, Fine - polyester talcs

MV Series (310, 305, 610, 607, 603) - talcs for coating industry

Clear Block 80 - anti-blocking additive in LDPE

Surface treated talcs (9603S, 9603Z) - S - silane treated (enhanced interaction), Z - zinc stearate treated (enhanced hydrophobicity)

XX 10, 07, 03, 02 - designed for polyolefins used in automotive and appliance

S.E.T., S.A., Leon, Spain

Specialty Minerals, Easton, PA, USA

PolyTalc AG Series AG

Vanderbilt, R.T. Company, Inc., Norwalk, CT, USA

Nyral 100, 200, 300, 400, 3300, 7700 - paints, coatings, polyolefins

IT FT, 3X, 5X, 325, X - rubber, plastics paints, and coatings

Vantalc 6H, F-2003 - plastics, rubber, paper and coatings applications

continued on the next page

MANUFACTURERS & BRAND NAMES:

Zemex Industrial Minerals, Atlanta, GA, USA

Benwood 2202, 2203, 2204, 2207, 2210, 2213 - high purity and brightness talc for industrial applications

Pioneer Talc - 767, 1599, 2606, 2620, 2630, 2655, 2661, 2664, 2720, 2871, 2882, 4304, 4306, 4316, 4317, 4319, 4320, 4392, 4404, 4411, 4416, MB-92 - Suzorite talcs for a broad range of applications

MAJOR PRODUCT APPLICATIONS: paper, paints, roofing, plastics, ceramics, animal feed, cosmetics, caulking, sound damping, putties, anti-caking agent, sealants, electrical insulation, plaster, lubricant, tile, appliances, garden furniture, food packaging, agricultural film

MAJOR POLYMER APPLICATIONS: PP, PE, PC, ABS, PPS, PS, rubber

Talc is the major constituent of rocks known as soapstone or steatite. Its paragenesis is associated with the hydrothermal metamorphism of siliceous dolomites, and thus it might be accompanied by tremolite, which may be of concern for many potential applications.

The composition of talc varies depending on its source. The most important factor is the amount of tremolite present. In the USA, for instance, Montana talcs are considered to be asbestos and tremolite free. The California plate-like talcs contain minor amounts of tremolite (less than 3%), whereas hard talcs contain between 5 to 25% tremolite. Some industrial talcs mined in upper New York State contain 25 to 50% tremolite. The other important component in its composition is water which is chemically combined in the magnesium oxide or brucite layer. Figure 2.62 shows the molecular structure of talc. Talc may lose this water only on

heating over 800°C but, if this happens, the plate-like structure is completely lost and talc properties are changed. The planar surfaces of the plate-like structure are held together by very weak van der Waals forces, and therefore talc can be delaminated at relatively low shearing forces, which accounts for the slippery feel of talc, and makes it easy to disperse.

Its plate-like structure provides talc-filled materials with

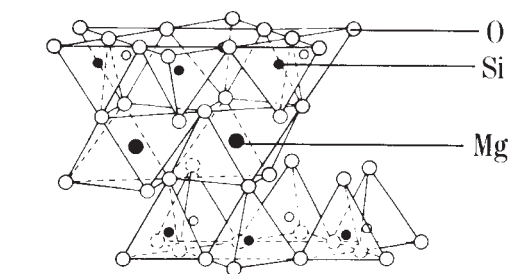


Figure 2.62. Molecular structure of talc. Courtesy of Luzenac Europe, Toulouse, France.

important properties, such as, high resistivity and low gas permeability. This comes about because the diffusion path is so complicated. Several other unique properties of talc are structure-related, including its lubricating effect, caused by its easy delamination; its low abrasiveness, because talc is the softest mineral in the Mohs hardness scale; and the hydrophobic properties of its surface. Hydrophobicity can be increased even more by surface coating with zinc stearate. Figure 2.63 shows the plate-like structure of talc.

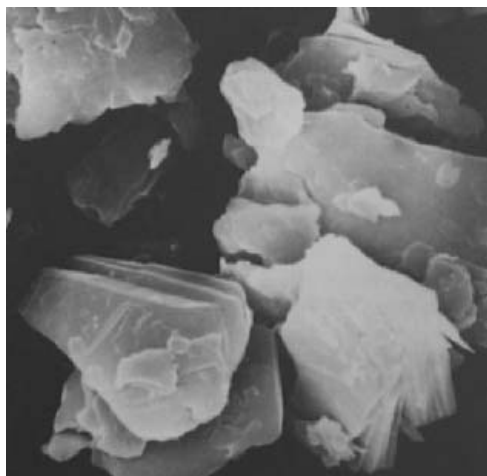


Figure 2.63. Minstron grade of talc. *Courtesy of Luzenac Europe, Toulouse, France.*

Talc processing is relatively simple. Emphasis is placed on the avoidance of contamination and on a sorting process to sort each talc variety according to mineralogy and color. Frequently manual and optical sorting are employed to obtain a high quality product.⁴⁵³ There is a wet and a dry process. Dry process begins with selective mining and sorting of the heterogeneous deposit. In the next stage, some ores may be blended and dried but all materials are subjected to grinding. Standard grinding on roller mills results in a coarse material (50 μm). Fine milling in impact mills produces, after classification, finer

grades (10–40 μm). The finest grades are obtained by micronization in jet mills (3–10 μm). The wet process separates by flotation those ores which contain a substantial amount of contamination (e.g., with carbonates). This results in materials having a very high concentration of pure talc (97–98%). Before flotation, the material is subjected to primary crushing in impact mill and bag milling which reduce particles to 100 μm . After flotation, the talc is filtered, dried and milled either by impact mills or by jet mill micronization. Some grades have silane surface treatment. The above description of the processes is based on production methods used by Luzenac in various plants worldwide.⁴⁵³

In the paper industry, talc was introduced as paper filler by Luzenac in 1905. The widespread use of talc is owed to ability to absorb organic materials, to prevent agglomeration, and to participate in the control of pitch. In recycled papers, talc reduces chemical content in paper manufacture. Talc imparts a smooth texture, reduces porosity and extends the life of machine components due to its lack of abrasiveness. Optimizing ink transfer, talc improves the quality of halftones.

In plastics, the addition of talc improves their heat distortion temperature, dimensional stability, scratch resistance, impact resistance, and reduces the process cycle due to nucleation. Other important properties include high brightness, blocking of infrared in agricultural film, anti-blocking properties, and low absorption of packaged components.

In paints, talcs have a high hiding power, a matting effect and give a satin finish. The morphological structure of talcs gives paints with low moisture permeability. Satin and matt finish in various types of paint is obtained through using talc.

2.1.55 TITANIUM DIOXIDE⁴⁷³⁻⁴⁸⁵

Name: titanium dioxide		CAS #: 13463-67-7
Chemical formula: TiO ₂	Functionality: depends on the surface composition	
Chemical composition: TiO ₂ - 80-99.5%, SiO ₂ - 0.15-1.1%, Al ₂ O ₃ - 0.3-3.9%, Fe ₂ O ₃ - 0.01-2%, ZrO ₂ - 0.4%		
Trace elements: Fe, Sn, Nb, Ta, Mg, Mn		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 3.3-4.25, 4.24 (pure rutile), 3.87 (pure anatase)		Melting point, °C: 1825
Thermal conductivity, W/K · m: 0.065	Loss on ignition, %: 0.1-2.3	
Coefficient of linear thermal expansion, 10 ⁻⁶ /K: 8-9.1	Mohs hardness: 6-7 (rutile), 5-6 (anatase)	
CHEMICAL PROPERTIES		
Chemical resistance: reacts with acids and alkalis		
Moisture content, %: 0.2-1.5	pH of water suspension: 3.5-10.5	Water soluble, %: 0.3-0.5
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 2.55-2.7	Tinting strength: 98-102	Brightness: 99-100
Relative scattering power: 64-108		
Dielectric constant: 114 (rutile), 48 (anatase)		Loss angle: 0.01-0.35
Brightness, L*: 93-98; Undertone, b*: -6 to -1.5 (gray tints), 1.0-1.9 (white tints)		
Color: white, buff		Resistivity, Ω-cm: 3000-9000
MORPHOLOGY		
Particle shape: acicular or spherical		Particle size, nm: 8-300
Crystal structure: tetragonal, orthorhombic, or trigonal in ore and tetragonal in final products		
Hegman fineness: 6-8	Oil absorption, g/100 g: 10-45	
Sieve analysis: 325 mesh residue: 0.01% to traces		Specific surface area, m ² /g: 7-162
MANUFACTURERS & BRAND NAMES: Degussa AG, Frankfurt/Main, Germany P25 - titanium dioxide obtained by pyrogenic process (the same method as used for fumed silica) having particle size of 21 nm and low pH (3.5-4.5) DuPont, Wilmington, DE, USA Hitox Corporation, Corpus Christi, TX, USA Hitox - titanium dioxide obtained by calcination with a small amount (2 wt%) of iron oxide produces buff color. It is economical pigment for coatings, caulks, adhesives, roofing and many plastics Kemira Pigments, Savannah, GA, USA		
continued on the next page		

MANUFACTURERS & BRAND NAMES:

Kronos, Toronto, Ontario, Canada

Anatase grades

Kronos 1001, 1002, 1077, E171 (no surface coating), 1014 (Al_2O_3 coating), 1015, 1071, 1075 ($\text{Al}_2\text{O}_3+\text{SiO}_2$ coating), 1074 ($\text{Al}_2\text{O}_3+\text{MnO}_2+\text{SiO}_2$ coating)

Plastics

Kronos 2075, 2200, 2210, 2230 (Al_2O_3 coating), 2073, 2220, 2222, 2257 ($\text{Al}_2\text{O}_3+\text{SiO}_2$ coating)

Coatings

Kronos 2059, 2063, 2063 S, 2300 (Al_2O_3 coating), 2043, 2044, 2047, 2056, 2057, 2160 ($\text{Al}_2\text{O}_3+\text{SiO}_2$ coating), 2190 ($\text{Al}_2\text{O}_3+\text{ZrO}_2$ coating), 2065 ($\text{Al}_2\text{O}_3+\text{SiO}_2+\text{ZnO}$ coating), 2310, 2330 ($\text{Al}_2\text{O}_3+\text{SiO}_2+\text{ZrO}_2$ coating)

Paper laminates

Kronos 2084, 2088 (Al_2O_3 coating), 2081 ($\text{Al}_2\text{O}_3+\text{SiO}_2$ coating)

Millennium Inorganic Chemicals, Baltimore, USA

*American Grades**Anatase grades*

A-2000, A-3000, A-3100 - products for paper, tire applications, and footwear

Paper

Tiona RCS-P (rutile slurry), HSS (anatase slurry)

Plastics

Tiona RLC-188 (phosphate and organic coating), RCL-4, RCL-69 (Al_2O_3 +organic coating), RCL-6 (Al_2O_3 and SiO_2 coating)

Coatings - architectural, automotive, coil and powder

Tiona RCL-9, RCL-535, RCS-9, RCS-535 (Al_2O_3 +organic coated), RCL-2, RCL-3, RCL-6, RCS-2, RCS-3 (Al_2O_3 and SiO_2 coating), RCL-628 (Al_2O_3 and ZrO_2 coating)

*Asia/Pacific Grades**Plastics*

Tiona RCL-188 (as above), RCL-69, RCL-128, RCL-181, RCL-575 (Al_2O_3 +organic coating), RCL-666 (Al_2O_3 , SiO_2 , organic coating)

Coatings - architectural, automotive, coil and powder, low VOC, inks

RCL-575, RCL-535, RCL-472 (Al_2O_3 +organic coating), RCL-373, RCL-6 (Al_2O_3 , SiO_2 coated), RCL-666 (Al_2O_3 , SiO_2 , organic coating), RCL-628 (Al_2O_3 , ZrO_2 , organic coating)

*European Grades**Plastics*

Tiona RLC-168 (as above), RCL-4, RCL-69, RCL-535 (Al_2O_3 +organic coated), RCL-6 ($\text{Al}_2\text{O}_3+\text{SiO}_2$ coated), RCL-168 ($\text{Al}_2\text{O}_3+\text{SiO}_2$ +organic coated)

Coatings - decorative, industrial, and special purpose

Tiona RCL-9 (Al_2O_3), RCL-472, RCL-535, RCL-552 (Al_2O_3 +organic), RCL-376, RCL-6 ($\text{Al}_2\text{O}_3+\text{SiO}_2$), RCL-388, RCL-666 ($\text{Al}_2\text{O}_3+\text{SiO}_2$ +organic), RCL-628 ($\text{Al}_2\text{O}_3+\text{ZrO}_2$ +organic)

Sachtleben Chemie, Duisburg, Germany

Hombitec RM 200, 220, 300, 400 - grades of transparent rutile grades having crystallite size in the range of 10-20 nm coated with Al_2O_3 or ZrO_2 . The product is designed to provide UV protection of coated substrates such as wood, plastics, etc.

TAM Ceramics, Inc., Niagara Falls, NY, USA

Heavy Grade Titanium Dioxide - a product designed for capacitors with a high density of 4.25 g/cm^3
continued on the next page

Tioxide Americas, Inc., Tracy, Canada

Anatase grade

A-HR - uncoated grade for paper, rubber, rubber latex, fibers, road markings, and ceramic systems

Rutile grades

R-Gran 850 - uncoated grade for optical glass and enamel and glaze frits

COMET 300, R-BC, R-FC6, R-HD6X, TR23, TR27, TR90 - Al_2O_3 coated grades for paper, PE, PP, PVC, ABS, PS, POM, PC, PPO, latex and alkyd paints, appliance enamels, vinyl wall covering, plastic pipe, wood finishes, interior coil coatings, metal decorative and appliance finishes, powder coatings

R-XL, TR50, TR60 - Al_2O_3 and SiO_2 coated for flat latex and alkyd paints, printing inks, colored PVC, exterior coil coatings, automotive finishes, exterior powder coatings

TR92 - Al_2O_3 and ZrO_2 coated is the pigment of choice for a very broad range of applications in paints, enamels, powder coatings and plastics including weather durable materials

TR93 - Al_2O_3 , SiO_2 , and ZrO_2 coated is the most resistant pigment which has high level of opacity, gives excellent gloss and the best UV durability

Ultrafine grades - transparent titanium dioxide for UV protection can be used with other pigments at 1% PVC

MAJOR PRODUCT APPLICATIONS: coatings, plastics, paper, inks, ceramics, capacitors, cosmetics, food, pharmaceuticals, fibers, white concrete, UV stabilizer; the products are not listed considering that most products use titanium dioxide

MAJOR POLYMER APPLICATIONS: PA, PVC, PE, PP, PPO, POM, PC, PS, ABS, polyester, acrylics, alkyd, polyurethane, melamine, phenoxy

Titanium dioxide is the most popular pigment used today. The first commercial pigment became available only in 1916 although titanium dioxide was chemically identified first in 1791.⁴⁸³ Coatings are the largest consumer of titanium dioxide using 57% of the production output, followed by plastics (20%), paper (13%), inks (3%) and ceramics (2%). All other applications accounted for only 5% of global use in 1996. In 1996, a total of 3.3 million tons was produced. Five companies contribute to satisfying 75% of this demand. If the merger between DuPont and Tioxide is approved, DuPont will hold 35% market, followed by Millennium (15%), Kronos (10%), Kerr-Mc-Gee (8%) and Kemira Pigments (7%).

The demand for titanium dioxide is based purely on its physical characteristics. Pigments have two prime functions: to color and to opacify. The coloring characteristics of the pigment depends on its ability to reflect incoming light. Magnesium oxide has the ability to reflect visible light more efficiently than titanium dioxide but it is still an inefficient pigment compared with TiO_2 because its capability to opacify is low. Opacifying capability depends on the refractive index and on the absolute difference between the refractive indices of the pigment and the matrix (binder). The most frequently used polymers have refractive indices between 1.45 and 1.6. White powders are considered to be useful as pigments if their refractive index is above 1.7. Titanium dioxide has refractive index between 2.55 (anatase) and 2.7 (rutile). The refractive index of titanium dioxide is higher than any other commercial white pigment. This combined with its reflecting capabilities makes it the most efficient pigment. (It should be noted that air has also very good pigmenting values because its refractive index is 1 which also produces a

large difference between it and typical matrices – larger than for zinc oxide, barium sulfate, calcium carbonate).^{479,483} The brightness and undertone of pigments depend on their light scattering ability. The brightness is determined by the intensity of reflectance and the undertone by the spectrum of reflected light (ratio of short to long wavelength of reflected light). The difference between anatase and rutile is in their undertone (anatase reflects more short wavelength and has a bluish undertone).

The particle size also has an important influence on the performance of titanium dioxide both as a pigment and as a UV absorber. For the pigment to have maximum opacity, the particle diameter must be equal to half of the wavelength (for a blue/green light to which the eye is most sensitive, the average wavelength is 460 nm, thus a particle diameter of 230 nm gives the maximum opacity). The color of the matrix (binder) has an influence here as well and titanium dioxide must compensate. For this reason, some grades of titanium dioxide are tailored to specific conditions and some are used to eliminate a yellow undertone. This is done by the choice of particle size. For this reason, commercial grades have particle sizes in a range from 200 to 300 nm. The amount of titanium dioxide is also crucial. If too little titanium dioxide is added, the distance between particles is too large and there is no enough opacity. If the amount is too great, it results in lower efficiency due to a particle crowding effect which causes particles to interfere in each other's scattering efficiency. Finally, good dispersion is critical since particles will only give their best performance when they are evenly distributed and separated by binder.

Titanium dioxide is obtained from the following minerals: rutile, anatase, brookite, and ilmenite. The first three minerals contain mostly TiO_2 , and their structure is octahedral. Both rutile and anatase are tetragonal, the difference being in the mutual arrangement of the octahedra, whereas brookite is orthorhombic. Rutile is the most common mineral, and its geological formation is associated with high temperature. Therefore, it is frequently found in company with other rocks also formed during a secondary high temperature process. Anatase and brookite are found in deposits formed from leaching of gneisses or schists by hydrothermal solutions. Anatase and brookite are converted to rutile upon heating to temperatures above 700°C . Trigonal ilmenite is an earlier constituent of a magma crystallization. By chemical composition, ilmenite is a titanate of ferrous iron. The color of the minerals ranges from yellowish to brownish. Other typical metals, present in small amounts, include Fe, Sn, Nb, Ta, Mg, and Mn.

Figures 2.64-2.66 show the crystalline structures of brookite, rutile, and anatase, respectively.

Most titanium dioxide is produced from ilmenite, which is in abundance. Two processes are used: sulfate and chloride processes. An ilmenite concentrate is reacted with concentrated sulfuric acid in an exothermic reaction. Ferric iron, which is a soluble form under these reaction conditions, is reduced to ferrous. The

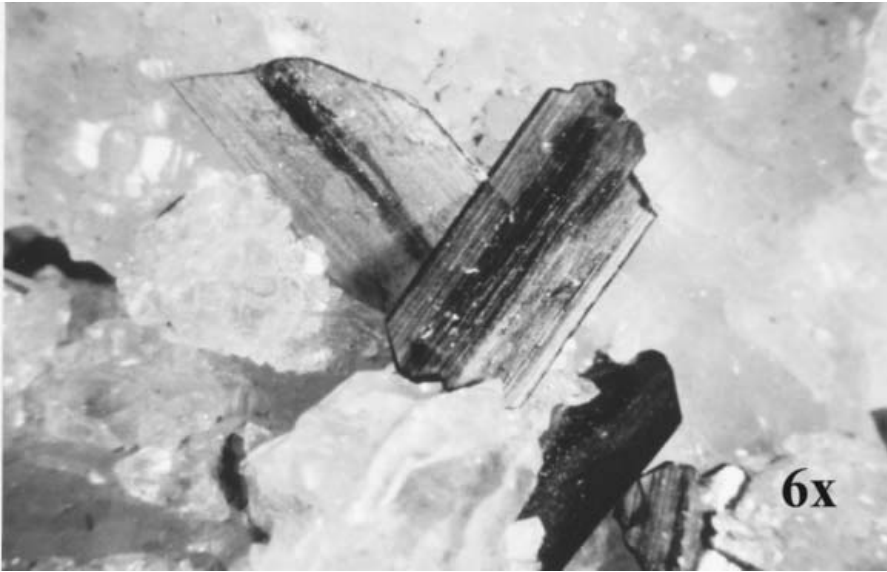


Figure 2.64. Brookite. *Courtesy of Tioxide Group PCL, London, UK.*

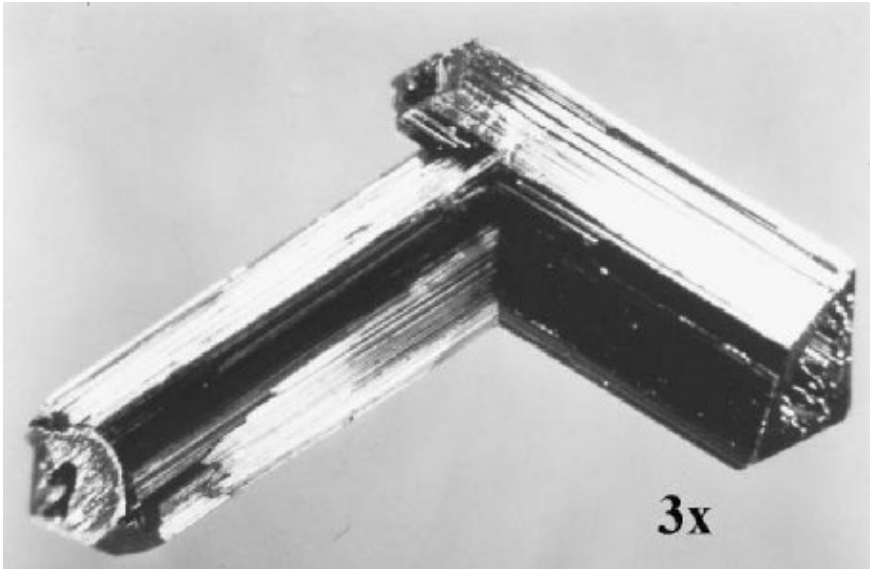


Figure 2.65. Rutile. *Courtesy of Tioxide Group PCL, London, UK.*

undissolved ore and the precipitated iron are removed as contamination. Titanium is precipitated in the form of hydrous titanium oxide after careful nucleation. The precipitate is separated by filtration and washed free of the mother liquor, which removes the traces of iron which would affect color. The washed precipitate is calcinated in a rotary kiln. This process may be followed by the addition of other

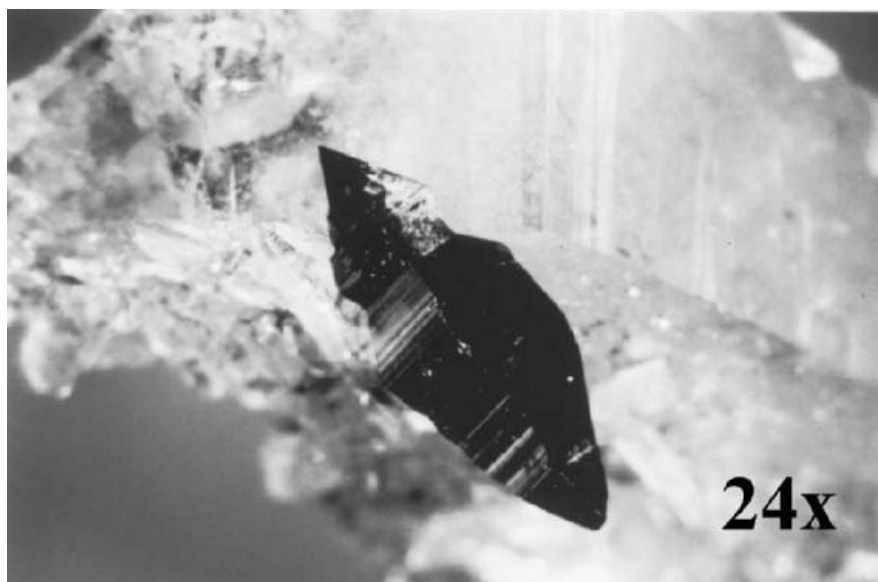


Figure 2.66. Anatase. *Courtesy of Tioxide Group PCL, London, UK.*

mineral components to modify properties. Finally, the product is ground and classified. Two processes, nucleation and calcination, determine the crystalline structure formation (e.g., rutile or anatase).

Titanium dioxide is also obtained from the chloride process, which gives an additional option to either hydrolyze titanium tetrachloride with steam or oxidize it with air to the dioxide. In this method, the pigment can be obtained from the gaseous phase. In this method, the feedstock must contain 90% rutile ore. It is not always possible to find such an ore therefore beneficiated feedstock is used which is obtained by various routes. Figure 2.67 compares both manufacturing processes.

The anatase form is manufactured using the sulfate process. The type of crystal (anatase or rutile) produced by the sulfate process depends on the conditions of the process. Generally both crystalline types are produced. The chloride process is used for the production of rutile pigment. New production lines are almost exclusively built for the chloride process because it produces titanium dioxide of higher purity and the operation results in less wastes and produces a smaller quantity of toxic materials. Uncoated rutile is produced in smaller quantities and used in other applications than paints and coatings. Anatase is produced frequently without a coating but Kronos does have a line of coated grades. An inorganic coating is applied in the aqueous slurry by precipitation of one or more hydrated metal oxides and by neutralization of acidic and alkaline compounds. The performance of the inorganic coating depends on the composition of coating (Al_2O_3 , SiO_2 , ZrO_2 , infrequently zinc and tin oxides), the amount of coating (1-15%, typically 5% for paint grades at thickness of 5 nm), the number of deposition stages, and the order and

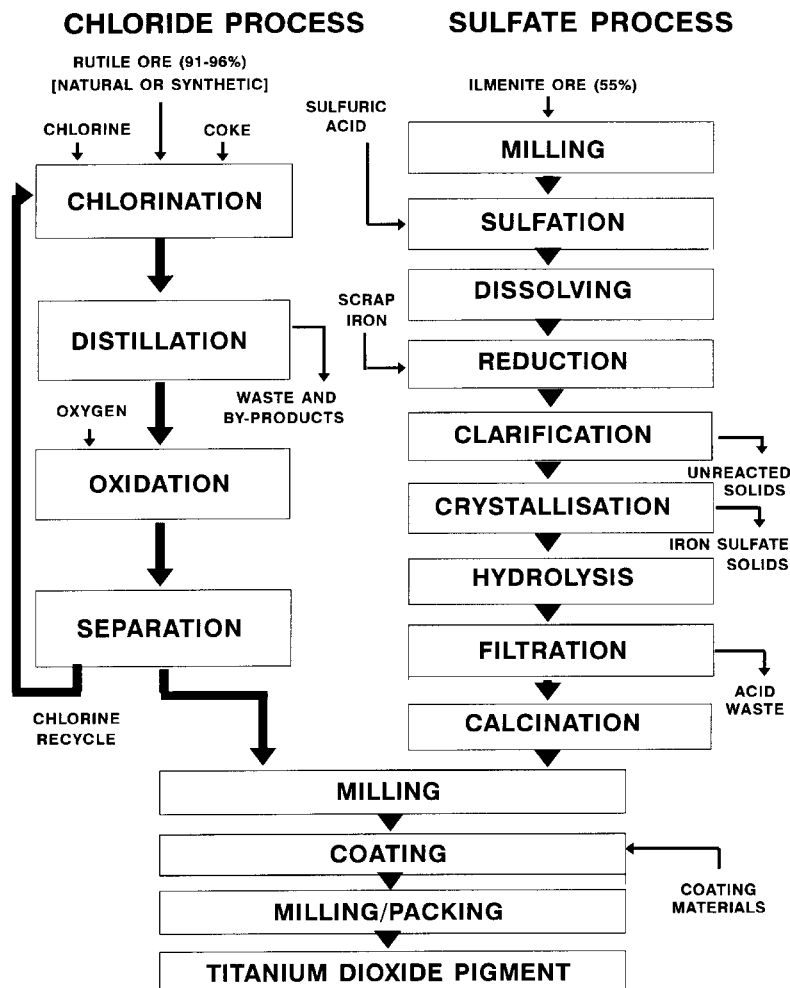


Figure 2.67. Schematic diagrams of chloride and sulfate processes of TiO₂ manufacture. *Courtesy of Millennium Inorganic Chemicals, Auburn, Australia.*

rates of deposition of the different coatings. The pH during deposition and after neutralization, the time given to the coating process, the temperature of the process and type of washing aids used all contribute to the performance of the coating and of the coated pigment. Although, zirconium oxide is used as a coating to improve weather stability, the choice of the type of coating used in given application is based on the requirements of the application. An organic treatment is performed to encapsulate particles with a monomolecular layer of a low polarity organic compound, typically trimethylol propane or pentaerythritol (0.3%). This treatment reduces the polarity of TiO₂ and improves its ease of dispersion.⁴⁸³

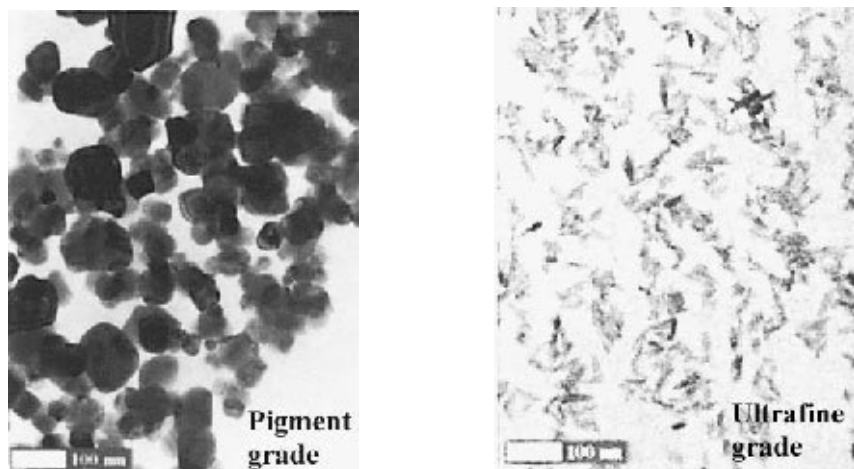


Figure 2.68. Comparison of pigment type and ultrafine titanium dioxide. *Courtesy of Sachtleben Chemie, Duisburg, Germany.*

Because the optimal light scattering of titanium pigments occurs when particle diameter is $0.24\ \mu\text{m}$, most pigments are manufactured to have the majority of particles closest to that in a range from 0.15 to $0.3\ \mu\text{m}$, depending on the application and the undertone required. Ultrafine grades are the exception. They typically have particle sizes in a range from 0.015 to $0.035\ \mu\text{m}$ and, because of their small particle size, they are transparent to visible light but absorb in the UV range. Ultralow particle size titanium dioxide is manufactured by Degussa by the same process as fumed silica. TiCl_4 is the raw material used in this process. Tioxide manufactures ultrafine TiO_2 by the wet process which begins from sodium titanate, Na_2TiO_3 , which is precipitated from a reaction with hydrochloric acid, neutralized by sodium dioxide, filtered, washed, milled and coated with SiO_2 , Al_2O_3 , ZrO_2 . Additional processes include, filtration and washing after coating, drying, micronizing, and packaging. The control over the process of precipitation affects the crystalline structure of the product. Both anatase and rutile can be obtained in either acicular or spherical morphology. The coating affects the photocatalytic activity of titanium dioxide. The ultrafine, uncoated grades have a high photocatalytic activity of $6.01\ \text{mol/g}\cdot\text{h}$. This can be reduced to $0.11\ \text{mol/g}\cdot\text{h}$ which is similar to that of the coated rutile used for pigment applications (0.07) and much lower than uncoated anatase pigment (0.87).⁴⁸¹ A broad range of properties can be obtained. Typically, surface area, particle size, and oil absorption can all be adjusted but the usual particle sizes are in a range from 7 to $35\ \text{nm}$ with surface areas and oil absorptions at the high end of the pigment titanium dioxide. The specific gravity is low at $3.3\ \text{g/cm}^3$. The size of the particle can be visualized from the comparison in Figure 2.68.

Figures 2.69-2.71 show the morphology of anatase pigment and rutile with and without coating. The layer of coating can be distinguished on micrograph.



Figure 2.69. Anatase titanium dioxide. *Courtesy of Tioxide Group PCL, London, UK.*

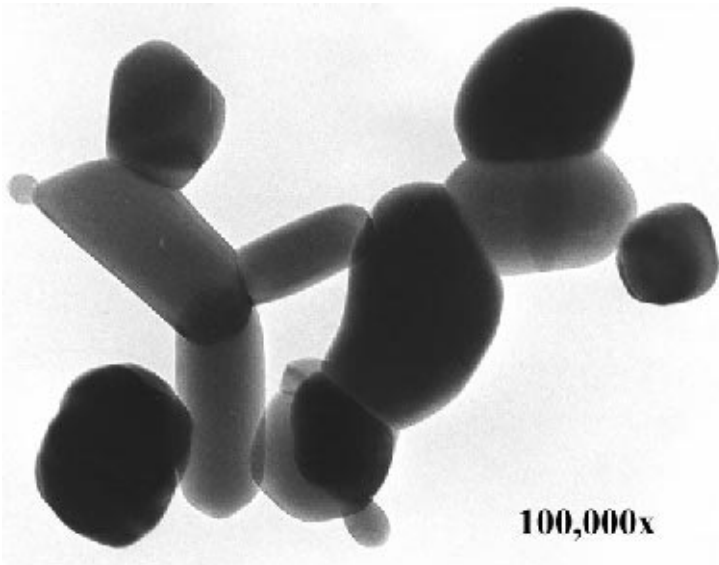


Figure 2.70. Uncoated rutile titanium dioxide. *Courtesy of Tioxide Group PCL, London, UK.*

In addition to the photochemical activity of titanium dioxide, grades have been developed for many other reasons discussed below. Millennium developed its Tiona RCL-188 grade for high performance extrusion. A surface treatment based on phosphate and an undisclosed organic material lowers the energy required for the process, improves the dispersion of pigment even at very high concentrations and without the addition of process aids. When stearates are used in formulation

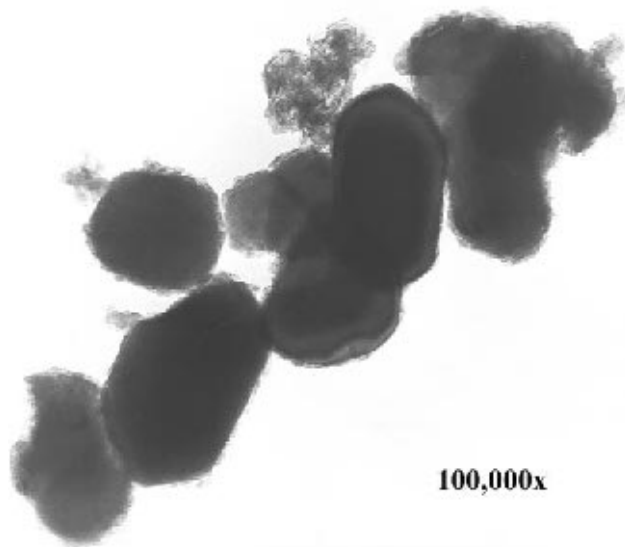


Figure 2.71. Coated rutile titanium dioxide. *Courtesy of Tioxide Group PCL, London, UK.*

there is the potential problem of overlubrication, Tiona RCL-188 does not suffer from this drawback. The surface properties of this grade are compatible with numerous polymers which makes it the material of choice in plastic extrusion applications. The Tiona RLC-4 grade from Millennium coated with a composite organic and Al_2O_3 coating is also compatible with numerous polymers. In addition, it is formulated to lower polyethylene yellowing. The product has excellent dispersion characteristics, a low melt flow index, and high tinting strength.

Incorporation of titanium dioxide into paints and coatings depends the grade of TiO_2 and on processing conditions. The pigment should be evaluated in the chosen formulation, considering that the final result depends on the quality of dispersion which, in turn, is affected by the pigment, dispersing agent type and amount, and the conditions of mixing. The investigation of this subject is outside the scope of this chapter.

In the paper applications, anatase form has an advantage over rutile in its reflection of light at wavelengths between 380 and 420 nm and on its effect on the abrasion resistance of the paper. The reflection of blue light increases the efficiency of optical brighteners. The scattering efficiency improves as particle size decreases. Tiona A-2000 is a very small particle size grade and, in addition, the slurry containing it has improved calcium resistance. A high concentration of titanium dioxide usually causes the slurry to thicken then gel over time when calcium carbonate is present. Tiona A-2000 is formulated to prevent viscosity changes of the coating slurry when calcium carbonate is added.

2.1.56 TUNGSTEN⁴⁸⁶

Name: tungsten powder		CAS #: 7440-33-7
Chemical formula: W	Functionality: none	
Chemical composition: W - 99.5-99.7%		
Trace elements: Al, Co, Cr, Cu, Fe, K, Mo, Ni		
PHYSICAL PROPERTIES		
Density, g/cm³: 19.35	Mohs hardness: 9	Melting point, °C: 3410
Thermal conductivity, W/K·m: 2.35	Specific heat, kJ/kg·K: 0.088	
CHEMICAL PROPERTIES		
Chemical resistance: soluble in HNO ₃ and HF		
OPTICAL & ELECTRICAL PROPERTIES		
Color: gray, black	Resistivity, Ω-cm: 5.6x10 ⁻⁶	
MORPHOLOGY		
Particle size, μm: 0.7-18	Crystal structure: cubic	
Sieve analysis: residue on 325 mesh sieve - traces		
MANUFACTURERS & BRAND NAMES: Teledyne Advanced Materials, Huntsville, AL, USA Tungsten powder C-3, C-5, C-6, C-8, C-10, C-20, C-40, C-60, crystalline - powders of different particle sizes (the higher the number the large the particle)		
MAJOR PRODUCT APPLICATIONS: composites		
MAJOR POLYMER APPLICATIONS: epoxy		

2.1.57 VERMICULITE

Name: vermiculite		CAS #: 1318-00-9
Chemical formula: (Mg,Fe ²⁺ ,Al) ₃ (Al,Si) ₄ O ₁₀ (OH) ₂ ·4H ₂ O		Functionality: OH
Chemical composition: SiO ₂ - 39.4%, MgO - 23.4%, TiO ₂ - 1.25%, Al ₂ O ₃ - 12.1%, Fe ₂ O ₃ - 5.5%, FeO - 1.2%, MnO - 0.3%, CaO - 1.5%, Na ₂ O - 0.8%, K ₂ O - 2.5%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.6	Specific heat, kJ/kg · K: 0.2	Melting point, °C: 1315
Thermal conductivity, W/K · m: 0.062-0.065		Maximum temperature of use, °C: 1100
Loss on ignition, %: 5.8		
CHEMICAL PROPERTIES		
Chemical resistance: insoluble in water and organic solvents		
pH of water suspension: 7	Adsorbed water, %: 240	
OPTICAL PROPERTIES		
Color: golden-brown		
MORPHOLOGY		
Particle shape: flakes (after expansion - concertina-shape granules)		Crystal structure: monoclinic
MANUFACTURERS & BRAND NAMES: Non-Metals, Inc., Affiliate of The China National Non-Metallic Minerals Group, Tucson, AZ, USA Chine Vermiculite Concentrate TG series - golden color, KV series - silver color Strong-Lite, Pine-Bluff, AR, USA expanded and non-expanded vermiculite for various applications		
MAJOR PRODUCT APPLICATIONS: insulation, construction, horticulture, paint, packaging, ion-exchange		

Vermiculite resembles mica in appearance. In industrial process, vermiculite flakes are rapidly heated at flame temperature approaching 1000°C. Some of the water of hydration is removed and the pressure generated by the water vapor expands (or exfoliates) vermiculite particles which increases in volume by 15 to 20 times. This expansion process must be precisely controlled to achieve the required expansion and to retain its water absorption properties. If the time of heating is extended, vermiculite will no longer absorb water. Thus, different grades may be produced by varying the heating time.

2.1.58 WOOD FLOUR AND SIMILAR MATERIALS⁴⁸⁷⁻⁴⁹¹

Names: wood flour, wood fiber, bark flour, wheat flour		CAS #: 9004-34-6
Chemical formula: variable		Functionality: OH
Chemical composition: protein content up to 15%		
PHYSICAL PROPERTIES		
Density, g/cm³: 0.4-1.35		Maximum temperature of use, °C: 200
CHEMICAL PROPERTIES		
Moisture content, %: 2-12	Adsorbed moisture, %: up to 20	Ash content, %: 0.5-0.7
pH of water suspension: 5		
OPTICAL PROPERTIES		
Color: buff, tan		
MORPHOLOGY		
Particle size, µm: 10-100	Oil absorption, g/100 g: 55-60	
MANUFACTURERS & BRAND NAMES: Ace International Inc., Centralia, WA, USA Douglas Fir Wood Flour - A-series (-20/100A, A-100A, A-200A), T-series (T-14, T-70, T-100) Alder Bark Flour - Modal regular light, regular dark, spray light, spray dark, superbond - used as glue extender in plywood industry for over forty years Wheat Flour - secondary extender in phenolic resin adhesives in plywood industry Agrashell, Inc., Bath, PA, USA Industrial Flour WF-5, WF-7 - nut shell flour American Wood Fibers, Jessup, MD, USA Hardwood grades 2010, 4010, 6010, 8010, 10010, 12010, 14010 - materials of different particle sizes Softwood grades 2020, 4020, 6020, 8020, 10020, 12020, 14020 - materials of different particles sizes		
MAJOR PRODUCT APPLICATIONS: sheet, pipes, automotive (door panels, air vents, under-dash parts, speaker brackets), toys, flower pots, lawn furniture, cosmetic packaging, garment hangers, brush blocks, paint roller and brush handles, paint pails, tool handles, computer accessories, office organizers, housewares, slats for blinds, speaker housings, vacuum cleaner beater bars, storage crates, toilet seats, pallets, chair supports, adhesives, brake pads, cosmetics		
MAJOR POLYMER APPLICATIONS: PP, PE, PVC, PS, polyester, poly(lactic acid), phenoxy, melamine		

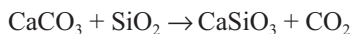
There are many applications for these fillers because they can improve dimensional stability, increase heat deflection temperature, reduce shrinkage, lower the weight of products, and reduce thermal expansion. Production costs are lowered also, because the wood flour is an inexpensive filler. In some applications, mechanical performance is improved as measured by impact strength and flexural modulus.⁴⁸⁸⁻⁴⁹⁰ The major drawback of these fillers is their hygroscopic nature which requires a long drying process to remove water prior to production. Their distinct color can be disadvantage but for some products it may be acceptable or even provide a desirable wood-like surface finish reducing the need for additional pigments.

2.1.59 WOLLASTONITE⁴⁹²⁻⁴⁹⁴

Name: wollastonite		CAS #: 13983-17-0
Chemical formula: CaSiO ₃		Functionality: from silane
Chemical composition: CaO - 43-47.5%, SiO ₂ - 44-52.2%, Fe ₂ O ₃ - 0.15-0.4%, Al ₂ O ₃ - 0.2-1%, MgO - 0.2-0.8%, MnO - 0.1%, TiO ₂ - 0.02%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.85-2.9	Mohs hardness: 4.5	Melting point, °C: 1540
Loss on ignition, %: 0.1-6		Coefficient of expansion: 6.5x10 ⁻⁶
CHEMICAL PROPERTIES		
Moisture content, %: 0.02-0.6	pH of water suspension: 9.8-10	Water solubility, %: 0.01
OPTICAL PROPERTIES		
Refractive index: 1.63	Color: white	Brightness: 80-94
MORPHOLOGY		
Particle shape: acicular	Crystal structure: monoclinic/anorthic (triclinic)	
Particle length, μm: 8-650	Oil absorption, g/100 g: 19-47	Hegman fineness: 0-7
Aspect ratio: 4-68	Particle thickness, μm: 1-50	
Sieve analysis: 325 mesh sieve residue - 0.09-3%		Specific surface area, m ² /g: 0.4-5
MANUFACTURERS & BRAND NAMES: Fibertec, Bridgewater, MA, USA Micronite AP, 1250S, 325, 200S - materials of different particle dimensions and aspect ratios Non-Metals, Inc. Affiliate of The China National Non-Metallic Minerals Group, Tucson, AZ, USA Wollastonite powder LST1, 2, 3, 4, LSP 1, 2 - grades of different brightness and fineness Nycor Minerals, Willsboro, NY, USA Nycor R, Nyad G, 200, 325, 400, 1250 - grades having different particle sizes and aspect ratios Wollastocoat 10, 400, Nyad G - surface modified grades Nyglos 4, 5, 8 - grades having different particle sizes and aspect ratios Quarzwerke GmbH, Frechen, Germany Tremin 283 - grades 010, 100, 400, 600, 800 (the higher the number the smaller the particle size) with different silane coating (AST - aminosilane, EST - epoxysilane, MST - methacrylsilane, TST - methylsilane, VST - vinylsilane) Tremin 939 - grades 100, 300, 600 (the higher the number the smaller the particle size) with different silane coating (AST - aminosilane, EST - epoxysilane, FST - alkylsilane, MST - methacrylsilane, ESST - epoxysilane special, USST - aminosilane special) Vanderbilt R.T. Company, Inc., Norwalk, CT, USA Vansil W-10, W-20, W-30		
MAJOR PRODUCT APPLICATIONS: coatings, primers, ceramics, adhesives, abrasives, insulating materials, sealants, wallboards		
MAJOR POLYMER APPLICATIONS: alkyd, acrylics, polyurethanes, epoxy, PP, PA, LCP, PET, SAN, PMMA, fluororubber, phenoxy		

Wollastonite is the industrially important mineral of the pyroxene mineral group. It occurs chiefly as a metamorphic mineral in crystalline limestones. Wollastonite has

been formed in reaction:



For this reaction to occur, a temperature above 450°C is needed to initiate the reaction between calcite and silica. Depending on the composition of minerals in the area where wollastonite was formed, materials with various levels of contamination resulted. The wollastonite mined in New York state can be converted to a high purity product (97-98%) because it contains garnet and diopside as associated minerals. These minerals can be magnetically removed. But calcite, which is a frequent admixture, is very difficult to remove. Wollastonite is the only naturally occurring white mineral which is wholly acicular. The length to diameter ratio (aspect ratio) typically varies from 3:1 to 20:1 but higher aspect ratios are also available. Wollastonite production consists of mining, grinding, separation, classification, and, with some products, treatment with a coupling agent. Commercially available fillers have an aspect ratio similar to the mineral, ranging from 3:1 to 20:1, an average particle diameter of 3.5 µm, and an equivalent spherical diameter distribution in a range from 0.3 to 40 µm. Figure 2.72 shows the morphology of wollastonite filler.

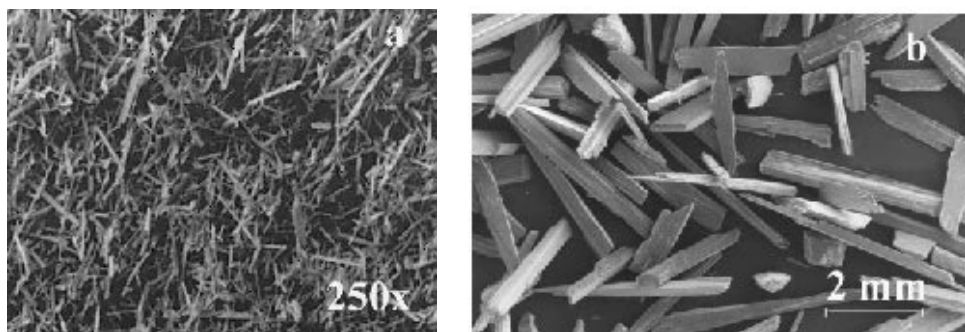


Figure 2.72. SEM micrographs of wollastonite. Courtesy of NYCO Minerals, Inc. Willsboro, NY, USA (a) and ECC International, St. Austell, UK (b).

Its specific surface area is very low (0.8-4 m²/g), indicating that the material is not porous. Other characteristic features of wollastonite include a high pH value (9.8), a low coefficient of thermal expansion (6.5×10⁻⁶/°C), and a low moisture content (less than 0.5%). Wollastonite is becoming an increasingly important filler as an asbestos replacement but its most important applications are due to its high brightness, low oil absorption, and reinforcing effect. In latex coatings, its high pH helps in stabilizing pH of the latex which improves the stability and shelf-life of the paint.

In plastics applications, wollastonite reinforces, increases scratch resistance, improves thermal stability, increases welding strength, and decreases warpage and

shrinkage. Figure 2.73 demonstrates the effect of surface treatment on reinforcement. In comparative room temperature evaluation of the surface treated and untreated wollastonite as a filler in polypropylene, the surface treated filler was firmly embedded in the matrix whereas the untreated wollastonite delaminated from the matrix. When fractured in liquid nitrogen the samples showed good adhesion between the matrix and surface treated wollastonite whereas untreated wollastonite had small gaps between the matrix and filler.

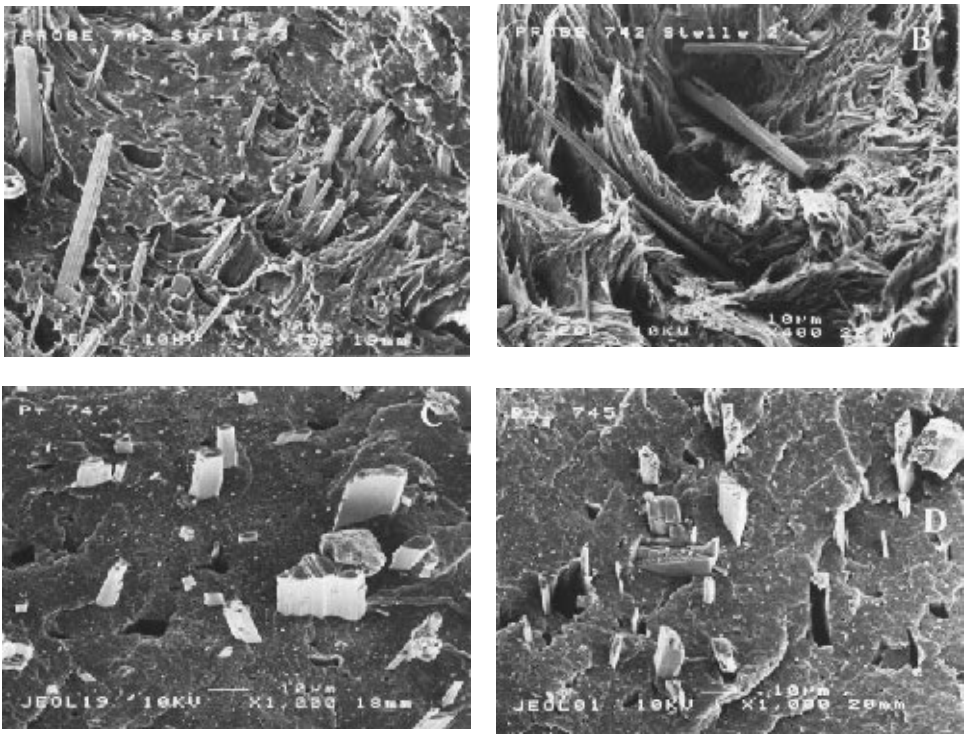


Figure 2.73. SEM micrographs of polypropylene fracture area. Top - fracture at room temperature, bottom - fracture at liquid nitrogen. left - surface treated wollastonite, Tremelin 939, right - untreated wollastonite, Tremelin 939. Courtesy of D. Skudelny, Quarzwerke GmbH, Frechen, Germany.

2.1.60 ZEOLITES⁴⁹⁵⁻⁴⁹⁸

Names: zeolite, molecular sieves		CAS #: 68989-
Chemical formula: variable		Functionality: OMe
Chemical composition: alkali aluminosilicate		
CHEMICAL PROPERTIES		
Cation type: K, Na, Ca		
Moisture content, %: 1.5	Adsorbed moisture, %: 23-29	pH of water suspension: 10-12
OPTICAL PROPERTIES		
Color: white		
MORPHOLOGY		
Particle size, μm: 50	Oil absorption, g/100 g: 30-42	Pore size, \AA: 3-10
Hegman fineness: 5-6		
MANUFACTURERS & BRAND NAMES: PQ Corporation, Valley Forge, PA, USA PQ Sieves - molecular sieves Valfor - zeolites Zeochem, Louisville, KY, USA Purmol 3A, 3ST, 4A, 5A, 13 - molecular sieves of different pore sizes		
MAJOR PRODUCT APPLICATIONS: plastics, coatings, sealants, caulks, adhesives, pigments, solvents, insulated glass, paper, primers, membranes		
MAJOR POLYMER APPLICATIONS: polyurethanes, polysulfides, PSF, PEI, PPO, PI		

Zeolites have found two major applications in polymeric systems: as selective membranes and as *in situ* drying agents. In moisture sensitive systems such as polyurethanes and polysulfides, molecular sieves help to scavenge moisture which extends the shelf-life of moisture cured products manufactured from these polymers. In these applications, 3 \AA molecular sieves are safe to use without special precautions because they contain no gas in their pores. Larger pore size sieves should be added under the vacuum to remove gas from the pore volume.

Molecular sieves are also used to scavenge moisture to prevent its condensation in insulated glass units. They are added to adhesive spacers or contained within the spacer which divides the glass panes. The spacer is a barrier to the penetration of the ambient atmosphere into the enclosed space of insulated glass unit.

Molecular sieves can be incorporated in one of two commercial forms: as a powder or as a dispersion in various organic media such as oils or plasticizers.

2.1.61 ZINC BORATE⁴⁹⁹

Name: zinc borate		CAS #: 1332-07-6
Chemical formula: 2ZnO ₃ ·B ₂ O ₃ ·3.5H ₂ O		Functionality: OH
Chemical composition: ZnO - 37.45%, B ₂ O ₃ - 48.05%, H ₂ O - 14.5%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 2.8		Melting point, °C: 980
CHEMICAL PROPERTIES		
Moisture content, %: 0.4-0.5	pH of water suspension: 8.1-8.3	
OPTICAL PROPERTIES		
Refractive index: 1.59	Color: white	
MORPHOLOGY		
Crystal structure: triclinic or amorphous		Specific surface area, m ² /g: 10-15
Particle size, μm: 0.6-1	Oil absorption, g/100 g: 37-44	
MANUFACTURERS & BRAND NAMES: Alcan Chemicals Europe, Gerrards Cross, UK Flamtard Z10 & Z15 - number is equivalent to the specific surface area		
MAJOR PRODUCT APPLICATIONS: flame retarding compositions of polymers listed below		
MAJOR POLYMER APPLICATIONS: PA, PPO, PC, PVC, PE, EVA, EPDM, polychloroprene, polyesters, epoxy		

Zinc borate is an inorganic flame retardant which can be used by itself or in combination with aluminum hydroxide or magnesium hydroxide with which it forms synergistic mixtures of high performance flame retardants. It is frequently used as a surface coating on these two fillers. It reduces smoke emission and promotes char formation.

2.1.62 ZINC OXIDE⁵⁰⁰⁻⁵⁰²

Name: zinc oxide		CAS #: 1314-13-2
Chemical formula: ZnO		Functionality: none
Chemical composition: ZnO - 99.5-99.9%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 5.6	Mohs hardness: 4	Melting point, °C: 1975
OPTICAL PROPERTIES		
Refractive index: 2.0	Color: white	Brightness: 90-94
MORPHOLOGY		
Particle shape: spherical	Crystal structure: hexagonal	Particle size, μm: 0.036-3
Oil absorption, g/100 g: 10-20	Specific surface area, m ² /g: 10-45	
MANUFACTURERS & BRAND NAMES: Nanophase Technologies Corporation, Burr Ridge, IL, USA NanoTek zinc oxide - nanoparticle size zinc oxide manufactured by physical vapor synthesis process Societe des Blancs de Zinc de la Mediterranee, Marseille, France Cachet Or - French process zinc oxide Zinc Corporation of America, Monaca, PA, USA Kadox - French process zinc oxide		
MAJOR PRODUCT APPLICATIONS: paints, coatings, crosslinker of rubber, sealants		
MAJOR POLYMER APPLICATIONS: acrylics, PVC, PC, PE, PP		

Zinc oxide is produced either by the French or by the American process. Both processes are pyrometallurgical techniques in which the metal in a vapor state reacts with oxygen, forming zinc oxide. The difference between the methods is in the raw material used for the synthesis. In the French process, pure metal is evaporated, and the final product is as pure as the metal used for its production. In the American process, zinc vapor is obtained directly from an ore by burning it as a mixture with coal or in an electrothermic process where electric current provides the heat. More recently, a new method, somewhat similar to the French process, was introduced by Nanophase Technologies Corporation who patented a physical vapor synthesis process in which zinc metal is vaporized. The vapor is rapidly cooled in the presence of oxygen, causing nucleation and condensation of nanoparticle size zinc oxide. The particles are non-porous and free of contamination.

Figure 2.74 shows the morphology of nanoparticle size zinc oxide which can be compared with zinc oxide obtained in French process (Figure 2.75).

The purest grades of zinc oxide from the French process contain more than 99.99% of ZnO. The purity of zinc oxide is essential in many applications because ZnO is a photochemically active material and impurities may severely affect its properties. Zinc oxide has found many applications due to its photochemical

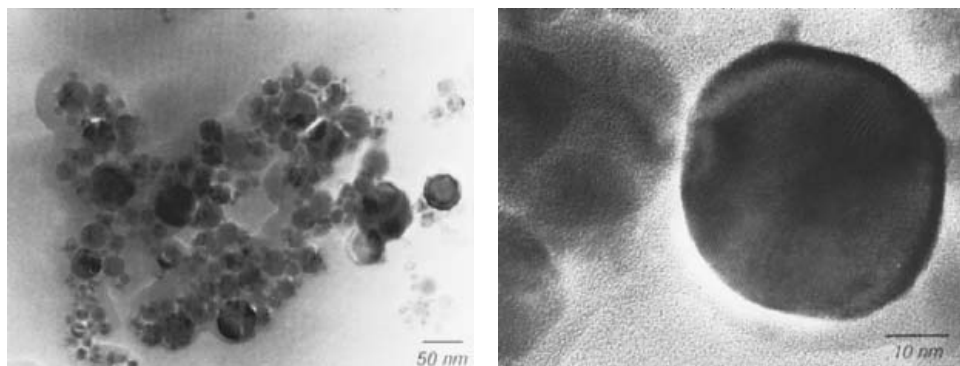


Figure 2.74. TEM micrographs showing NanoTec zinc oxide. *Courtesy of Nanophase Technologies Corporation, Burr Ridge, IL, USA.*

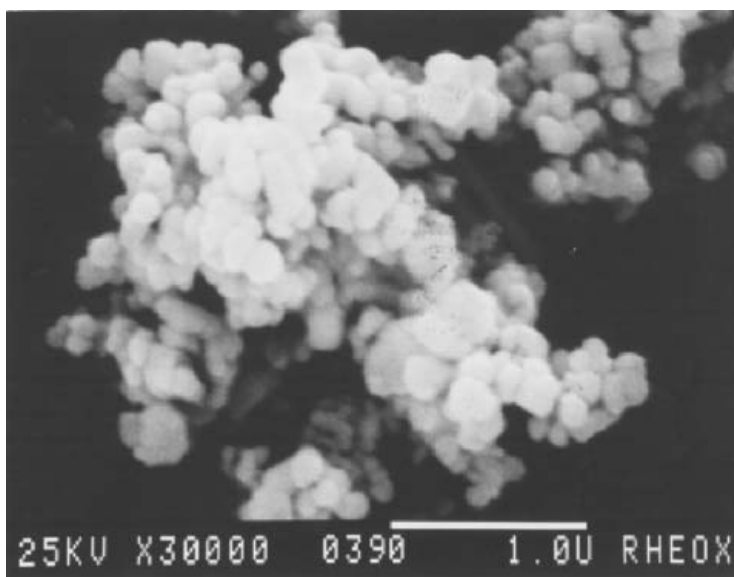


Figure 2.75. SEM micrographs of Kadox 915 manufactured by French process.

properties and chemical reactivity. One of the essential mechanisms of chemical reaction is that in which it forms zinc sulfides, thus preventing product discoloration.

Its particle size is usually in a range from 0.1 to 0.4 μm , and its specific surface area is correspondingly in a range from 20 to 10 m^2/g . Nanosize particles have an average particle size of 36 nm and a substantially higher specific surface area at 15–45 m^2/g . The high surface area is due to the small particle size, as zinc oxide has little porosity. A product having an average particle size of 0.11 μm has oil

absorption as low as 12 g/100 g. Some grades, especially those used in the rubber industry, can be surface modified, usually by the deposition of 0.2-0.4% of stearic acid, propionic acid, or light oil, all of which coatings facilitate mixing.

Several reasons are behind the widespread use of zinc oxide. Zinc oxide is a popular crosslinker for rubber and for various resins. Zinc oxide is also used as an UV stabilizer and as an additive having biocidal activity. It is frequently used in paints. Zinc oxide also has a relatively high refractive index which makes it an efficient white pigment.

2.1.63 ZINC STANNATE⁵⁰³

Names: zinc stannate, zinc hydroxystannate		CAS #: 12036-37-2 or 12027-96-2
Chemical formula: ZnSnO ₃ and ZnSn(OH) ₆		Functionality: OH
PHYSICAL PROPERTIES		
Density, g/cm ³ : 3-3.9	Decomposition temp., °C: 180-400	
CHEMICAL PROPERTIES		
Moisture content, %: 0.5	pH of water suspension: 9-10	
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 1.9	Conductivity, μS/cm: 800	Color: white
MORPHOLOGY		
Particle size, μm: 2.5		
MANUFACTURER & BRAND NAME: Alcan Chemicals Europe, Gerrards Cross, UK Flamtard S (zinc stannate), Flamtard H (zinc hydroxystannate), Flamtard HB1 (zinc hydroxystannate/zinc borate blend)		
MAJOR PRODUCT APPLICATIONS: flame retardant in the polymers listed below		
MAJOR POLYMER APPLICATIONS: PVC, PE, PA, EVA, EPDM, PC, polyesters, epoxy, polychloroprene		

Zinc stannate is an inorganic flame retardant which can be used by itself or in combination with aluminum hydroxide or magnesium hydroxide with which it forms synergistic mixtures of high performance flame retardants. It is frequently used as a surface coating on these two fillers. It reduces smoke emission and promotes char formation.

2.1.64 ZINC SULFIDE

Names: zinc sulfide		CAS #: 68611-70-1
Chemical formula: ZnS		Functionality:
Chemical composition: ZnS - 98%, ZnO - 0.2%, BaSO ₄ - 1%		
PHYSICAL PROPERTIES		
Density, g/cm ³ : 4	Mohs hardness: 3	Melting point, °C: 1700
CHEMICAL PROPERTIES		
Chemical resistance: not resistant to strong acids and alkalis		
Moisture content, %: 0.3	pH of water suspension: 6-7	
OPTICAL & ELECTRICAL PROPERTIES		
Refractive index: 2.37	Color: white	Brightness: 98
Tinting strength: 55-62% TiO ₂	Conductivity, mS/cm: 0.2	
MORPHOLOGY		
Particle size, μm: 0.3-0.35	Oil absorption, g/100 g: 13-14	Specific surface area, m ² /g: 8
Sieve analysis: residue on 325 mesh sieve - 0.001-0.01%		
MANUFACTURERS & BRAND NAMES: Sachtleben Chemie GmbH, Duisburg, Germany Sachtolith L (standard paints), HD (high quality paints), HD-S (plastics)		
MAJOR PRODUCT APPLICATIONS: paints, coatings, inks, UV-curable systems, powder coatings, adhesives, insulating and sealing compounds, fibers, paper, sealants, mastics, lubricants		
MAJOR POLYMER APPLICATIONS: alkyd, epoxy, acrylics, PVC, PE, PP, PS, PET, PA		

Zinc sulfide is produced by synthetic methods from pure zinc and sulfide obtained as a by-product of barium sulfate synthesis. The precipitated filler has a very small particle size which makes it unsuitable for use as a white pigment. The optimum particle size is obtained by calcination in a continuously operated kiln at 700-800°C. Zinc sulfide crystals grow under these conditions to 0.3 μm which is optimal for white pigment. Depending on the grade, the product of calcination is either deagglomerated or surface treated in a process similar to titanium dioxide. Figure 2.76 shows the morphology of the product obtained by this method.

Zinc sulfide has the next highest refractive index to titanium dioxide and zirconium oxide making it a very efficient pigment. The spectrum of absorption of zinc sulfide resembles more closely anatase than rutile. Because it does not absorb certain UV wavelength, zinc sulfide is useful as a pigment for UV curable materials.

Figure 2.76 implies that zinc sulfide causes low abrasion to the equipment because of its spherical shape and also because of low hardness. Its low oil number



Figure 2.76. SEM micrographs of zinc sulfide, Sachtolith, under three magnifications of 2000x, 10,000x and 150,000x. *Courtesy of Sachtleben Chemie GmbH, Duisburg, Germany.*

means that little binder is needed and minimizes its effect on viscosity of melts and dispersions.

In paint applications, zinc sulfide gives two advantages in addition to its function as a pigment: it gives anti-corrosive properties and acts as efficient algicidal agent. In addition, coatings can be formulated with a reduced level of rheological additives which further improves the anti-corrosive properties of primers.

In plastics applications, zinc sulfide is used for its flame retarding properties. Flame retardant products can be formulated free of antimony and bromine. Zinc sulfide can also be used as a partial replacement of antimony oxide.