

INDUSTRIAL APPLICATIONS OF KAOLIN

by

HAYDN H. MURRAY

Georgia Kaolin Company, Elizabeth, New Jersey

ABSTRACT

Kaolins are used in a multiplicity of industries because of unique physical and chemical properties. Shape, particle size, color, softness, and non-abrasiveness are physical properties that are especially important. Chemical properties, such as comparatively low base exchange capacity, as well as other chemical properties of the kaolin surface, and relative insolubility, are governing in many uses. In 1960, well over 2,000,000 tons of kaolin was used in the United States, more than one-half of which was consumed by the paper industry. The relationships between physical and chemical properties are discussed in the application of kaolin to paper, rubber, ceramics, plastics, ink, catalysis, insecticides, and numerous other uses. A few new uses of kaolin are discussed along with a short gaze into a crystal ball to see what the future may hold for that useful mineral, kaolin.

INTRODUCTION

The industrial mineral kaolin has many uses. It has favorable properties such as natural whiteness, fine particle size, non-abrasiveness, and chemical stability. Kaolinite is the proper name of the mineral about which this article is written, but in industrial terminology the mineral is known as kaolin, so all references will be to kaolin. The largest known deposits of kaolin in the United States are in Georgia and South Carolina. These deposits are sedimentary and occur as lenticular bodies in the Tuscaloosa Formation of Cretaceous Age (Murray, 1960, p. 280). Natural processes in the geologic past have segregated the kaolins and deposited them in relatively pure lenses. The kaolins vary in their degree of crystal perfection which affects many properties (Murray and Lyons, 1956; Murray and Lyons, 1960). For this and other reasons, the crude kaolin is tested extensively before the deposit is prepared for mining. The theoretical chemical composition of kaolin and a chemical analysis of a crude kaolin from Dry Branch, Georgia, shown below, indicate the relative purity of many of the Cretaceous kaolins in Georgia and South Carolina.

Two basically different processes are used to refine kaolins and remove the major impurities. The simplest process is called air flotation or the dry process. The properties of the finished product depend to a large extent on those properties inherent in the crude kaolin. In the dry process operation, a deposit must be chosen with desirable properties of color and relatively low

| | Theoretical kaolinite | Kaolin from Georgia |
|------------------|-----------------------|---------------------|
| Aluminum oxide | 39.8% | 38.38% |
| Silicon dioxide | 46.3 | 45.30 |
| Iron oxide | — | 0.30 |
| Titanium dioxide | — | 1.44 |
| Calcium oxide | — | 0.05 |
| Magnesium oxide | — | 0.25 |
| Sodium oxide | — | 0.27 |
| Potassium oxide | — | 0.44 |
| Ignition loss | 13.9 | 13.97 |

content of grit ($> 44 \mu$). The crude kaolin is transported to the mill where the large chunks are reduced to about egg size by roll crushers. The crushed kaolin is fed into rotary driers and then into airfloating equipment. The latter usually consists of a pulverizing unit and an air separator. The fine particles are transported to collecting chambers and the coarse particles are fed back into the pulverizer. Dry processing yields a product of relatively low cost.

The second process used to produce kaolins is much more complex and is called the wet process. The kaolin is dispersed in water after it is mined. The first step after dispersion is the removal of the coarse grit ($> 44 \mu$) by settling procedures and vibrating screens. The resultant degrittied slurry is fed into centrifuges to separate the kaolin into fine, intermediate, and coarse particle size fractions. These fractions can be chemically bleached to remove some coloration caused by iron impurities. The kaolin is then dewatered through a filtration process, dried in either rotary, apron or spray driers, and prepared for shipment. This process is used to produce highly refined kaolins having controlled properties.

Kaolin has many industrial uses. In addition to the general properties mentioned in the first paragraph, it is soft, has low viscosity at high solids content in many systems, is readily wet and dispersed in water and some organic systems, and can be produced with a controlled particle size distribution. Some of the important physical constants of kaolin are: specific gravity, 2.60; index of refraction, 1.56; hardness (Mohs scale), 2; fusion temperature, 1850°C ; dry brightness, 78–92 percent.¹

As mentioned previously many kaolins have a low viscosity at relatively high solids content. For example, many kaolins can be dispersed readily in water at 70 percent solids by weight and the resultant slurry pours like fresh milk. This is an attractive property for the paper coating industry as will be pointed out later.

The ranges of particle size distribution in which kaolins are produced commercially are shown in Fig. 1. Several end uses of kaolin depend upon the

¹ Measured at $458 m\mu$ on a General Electric recording spectrophotometer, against MgO reference.

particle size distribution. In many applications a coarse-particle kaolin may not work whereas a fine-particle kaolin will, and vice versa. Some of the more important industrial uses will be described in this paper, but it must be

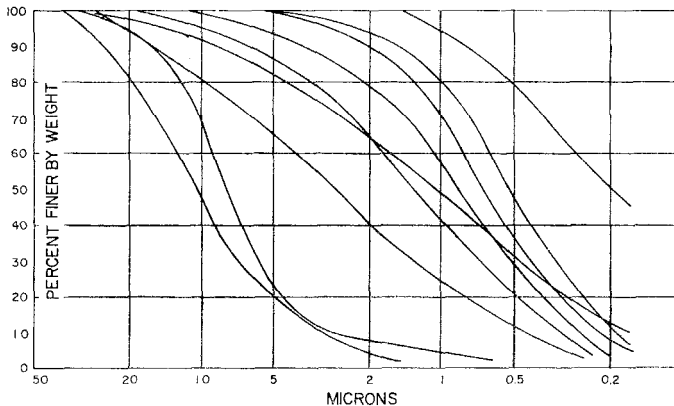


FIGURE 1.—Particle size distribution curves of commercially available kaolins.

realized that these descriptions, of necessity, are brief and incomplete. More than 2,000,000 tons of kaolin is used annually in the United States (de Polo, 1960, p.207).

The author wishes to acknowledge the help of Dr. Wayne M. Bundy and Mr. S. C. Lyons in the preparation of this paper.

INDUSTRIAL USES

Paper

The largest single user of kaolin is the paper industry, which used approximately 1,200,000 tons in 1958 (de Polo, 1960, p. 207). Because kaolin is used, paper products print better and are made whiter and smoother. Kaolin used as a filler in the interstices of the sheet adds ink receptivity and opacity to the paper sheet. Kaolin used to coat the surface of the paper sheet makes possible sharp photographic illustrations and bright printed colors. Kaolin constitutes nearly one-third the weight of today's slick sheet magazines. The significant properties of kaolin of greatest value to the paper industry are whiteness, low viscosity, non-abrasiveness, controlled particle sizes, and flat hexagonal plates. Opacity is an extremely important property to the paper industry and Fig. 2 shows the relationship between the particle size of the kaolin and opacity. Brightness, gloss, and viscosity properties also depend on particle size (Lyons, 1958, p. 81).

Flow properties or rheology of kaolin clays, especially the kaolin coating clays used in the paper industry, are very important because of their influence

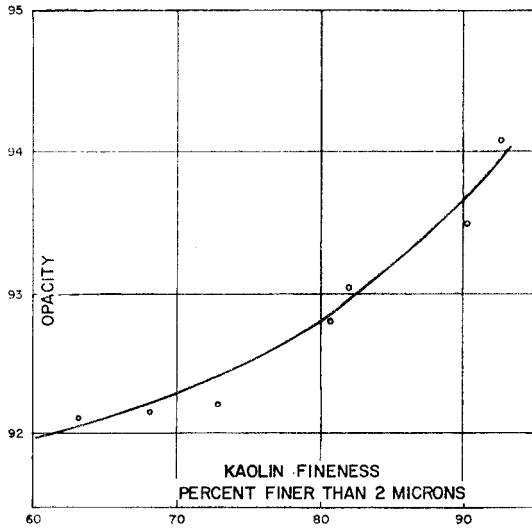


FIGURE 2.—Relationship between particle size of kaolin and opacity of coated paper. (Opacity is the ratio of the percent reflectance of a sheet of paper measured over a black background divided by the percent reflectance measured over a white background).

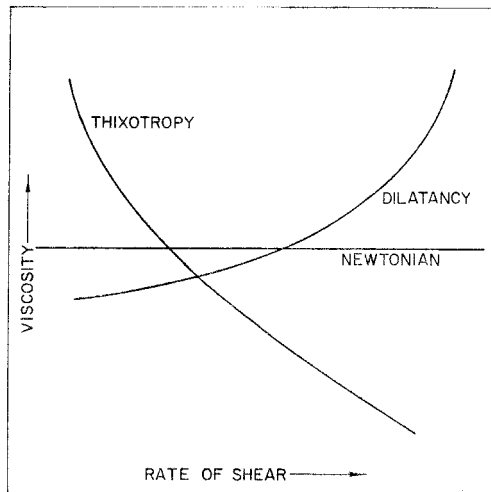


FIGURE 3.—Types of viscous flow that kaolin slurries exhibit.

on coat weight, smoothness, texture, and other properties. Figure 3 shows plots of viscosity vs. shear rate for Newtonian, thixotropic, and dilatant fluids. These three types of viscous flow are of primary interest to paper coaters. Particle size distribution, particle shape, electrokinetic effects between particles, presence of impurities and degree of flocculation and dispersion all affect rheology. Rheology of kaolin slurries has been the subject of several papers and patents in recent years (Albert, 1951, p. 456; Millman and Whitley, 1959; Murray, 1961).

If one were going to design in a laboratory a coating pigment for the paper industry, it would be white, disperse readily in water, and have low viscosity, be soft, have a fine particle size, and be a thin plate-shaped particle. Nature produced a mineral which has essentially all the above properties, and that mineral is kaolin. It can be readily seen why kaolin is an ingredient essential to the paper industry.

Rubber

Kaolin is used as a filler in many rubber goods. It adds strength, abrasion resistance, and rigidity to both natural and synthetic rubber products. In general, most rubber products extrude more easily after kaolin filler is added. The major reason that kaolin is used in rubber compounds is its whiteness and low cost. Although kaolin costs less than most other rubber pigments, it has excellent functional properties.

Ceramics

Kaolin is used in ceramic whiteware products, insulators, and refractories (Smoot, this Volume). In whitewares, kaolin aids accurate control of molding properties, and adds dry and fired strength, dimensional stability, and a smooth surface finish to the ware. The excellent dielectric properties and chemical inertness of kaolin make it well suited for porcelain electrical insulators. In refractory applications, the dimensional stability, high fusion point, and low water content, along with high green strength, make kaolin an important constituent.

Paint

Kaolin is used in paint because it is chemically inert and insoluble in the paint system, has a high covering power, gives the paint desirable flow properties, and is low in cost.

Plastics

The addition of kaolin to thermosetting and thermoplastic mixes gives smoother surfaces, a more attractive finish, good dimensional stability, and high resistance to chemical attack. In addition, the flat hexagonal kaolin plates hide the reinforcing fibers and give the mix flowability to simplify the molding of complex shapes.

Other Applications

Kaolin has many other industrial applications, some of which are listed here:

| | | |
|-----------------------|-------------|-------------------|
| ink | cement | detergents |
| adhesives | fertilizers | porcelain enamels |
| insecticides | plaster | paste |
| medicines | filter aids | roofing granules |
| food additives | cosmetics | sizing |
| catalyst preparations | chemicals | foundries |
| bleaching | crayons | linoleum |
| adsorbents | pencils | floor tiles |
| | | textiles |

Special Applications Through Chemical Modifications

Kaolin is hydrophilic and can be dispersed in water and in some other systems. Because of the nature of the chemistry of its surface, kaolin can be chemically modified so that it will become hydrophobic or organophilic, or both. Generally, an ionic or a polar non-ionic surfactant is used as the surface-treating agent.

Electrophoretic studies have shown that kaolin has an overall negative charge. The exchange capacity of kaolin results from broken bonds and isomorphous substitution of Al for Si in the tetrahedral sheet in the structure (Grim, 1953, p. 132). The exchange sites are the locations on the surface where polar molecules can be adsorbed and oriented.

The choice of surface treatment or chemical modification depends upon the polarity, structure, and composition of the organic system into which the kaolin is to be utilized and the physical and chemical properties desired in the end product.

Wetting, dispersion, flow properties, and general physical-chemical behavior are most important in the organic medium into which the kaolin is to be utilized. Thorough wetting of kaolin by the vehicle is essential in order to derive maximum utility and functionality. Wetting breaks down the attractive forces between kaolin particles and facilitates the coating of each particle with the wetting medium. Even though wetting is complete, dispersion will not necessarily be the ultimate, because the attractive forces between kaolin particles may still be effective across interfaces causing loose agglomeration of the particles.

Flow properties are closely related to wetting and dispersion. Interparticle attraction produced by unlike surface charges causes the formation of an internal structure which inhibits flow and gives rise to thixotropy (Michaels, 1958, p. 26). Uniform wetting and good dispersion tend to give flow properties which approach Newtonian and dilatant systems.

Improvements in functionality of kaolin fillers after surface modifications have been noted in the ink, paint, rubber, and plastics industries (Albert, 1960a, 1960b; Bundy, 1961; Felletschin, 1961; von Volkenburgh, 1959;

Werner, Marra, and Gilman, 1960; Wilcox, 1961a, 1961b). Dispersion is essential for smooth films with high finish and for improved color tone and texture. Decrease in viscosity by virtue of improved dispersion enables higher pigment loadings as well as easier workability.

Organophilic kaolins are being used in the rubber industry where it has been found that the modified kaolin is easier to incorporate in the polymer system, higher pigment loadings are obtained, and faster cure rates, higher modulus, and higher tensile strength can be achieved. In paints, plastics, and inks, organophilic kaolins are being used because they disperse and wet out rapidly, have better suspension properties, and give superior water resistance and reduced viscosities. In polyester resins, for example, some organophilic kaolins give viscosities tenfold less than viscosities obtained for unmodified kaolins of exactly the same particle size distribution and tested under similar conditions.

The future industrial use for surface-modified kaolins looks very good indeed. Additional research will find new and better surfactants for modifying the kaolin surface and new end uses will be forthcoming. Industrial applications for surface-modified kaolins will increase very rapidly in the next few years.

Calcined Kaolins

Another area that deserves mention is the large industrial use of calcined kaolin. When kaolin is heated to approximately 1050°C it is converted to mullite, cristobalite, and/or a silica alumina spinel (Brindley and Nakahira, 1959, p. 312). This calcined product is whiter and more abrasive than the original kaolin, and the surface chemistry and physical properties are completely changed. The largest utilization of calcined kaolins is in paint, rubber, and plastics.

SUMMARY

Kaolin is a unique industrial mineral that has properties that make it a functional ingredient in many industrial applications. The largest tonnage of kaolin is used by the paper industry. Surface-modified kaolins have a rosy industrial future. Research efforts in this area are disclosing new and fascinating uses. Calcined kaolins also are in demand particularly for paints, rubber, and plastics.

REFERENCES

- Albert, C. G. (1951) Particle structure and flow properties of coating clays: *TAPPI*, v. 34, pp. 453-458.
- Albert, C. G. (1960a) U.S. Patent 2,941,923.
- Albert, C. G. (1960b) U.S. Patent 2,948,632.
- Brindley, G. W. and Nakahira, M. (1959) The kaolinite-mullite reaction series; I. A survey of outstanding problems: *J. Amer. Ceram. Soc.*, v. 42, pp. 311-324.
- Bundy, W. M. (1961) Brit. Patent 867,752.

- Felletschin, G. (1961) U.S. Patent 3,000,750.
- Grim, R. E. (1953) *Clay Mineralogy*: McGraw-Hill, New York, 384 pp.
- Lyons S. C. (1958) Clay (kaolin): in *Paper Coating Pigments*, TAPPI Monograph Series, no. 20, pp. 57-115.
- Michaels, A. S. (1958) Rheological properties of aqueous clay systems: in *Ceramic Fabrication Processes*, W. D. Kingery, ed., pp. 23-31.
- Millman, N. and Whitley, J. B. (1959) U.S. Patent 2,907,666.
- Murray, H. H. (1960) Clay: in *Industrial Minerals and Rocks*, AIME, pp. 259-284.
- Murray, H. H. (1961) U.S. Patent 2,995,458.
- Murray, H. H. and Lyons, S. C. (1956) Correlation of paper-coating quality with degree of crystal perfection of kaolinite: in *Clays and Clay Minerals*, Nat. Acad. Sci.-Nat. Res. Council, pub. 456, pp. 31-40.
- Murray, H. H. and Lyons, S. C. (1960) Further correlations of kaolinite crystallinity with chemical and physical properties: in *Clays and Clay Minerals*, Pergamon Press, New York, pp. 11-17.
- de Polo, T. (1960) Clays: in *Mineral Facts and Problems*, U.S. Bur. Mines, Bull. 585, pp. 199-212.
- Smoot, T. W. (1963) Clay minerals in the ceramic industries: This volume.
- von Volkenburgh, R. (1959) U.S. Patent 2,890,190.
- Werner, T. H., Marra, W. H. and Gilman, W. B. (1960) U.S. Patent 2,949,397.
- Wilcox, J. R. (1961a) U.S. Patent 2,982,665.
- Wilcox, J. R. (1961b) U.S. Patent 2,999,808.