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DIAGNOSTIC TESTS FOR EVALUATION OF KAOLIN PHYSICAL PROPERTIES

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ABSTRACT

Kaolin is an important industrial mineral which is used by many process industries including paper, paint, plastics, ceramics, rubber, and many others. Several standard tests must be performed to fully evaluate the economic potential of kaolin. These include mineralogical determinations by X-ray diffraction, scanning electron microscopy, differential thermal analysis, and the petrographic microscope; particle size distribution; grit percentage (material larger than 44 microns); color (brightness and whiteness); viscosity; resistivity; particle shape; beneficiation response (chemical leaching, flotation, high intensity magnetic separation); ceramic tests (green, dry, and fired strength, shrinkage, fired color, porosity, fusion temperature); and surface area. Other tests that are used include oil absorption, gloss, opacity, abrasion, moisture, pH, reagent demand, and others.

INTRODUCTION

Kaolin is one of the most versatile of the industrial minerals [MURRAY, 1977] in that it is so extensively used for so many applications [MURRAY, 1963]. Many new uses are being discovered for this versatile mineral each year. It is a unique industrial mineral because, except for catalytic activity in some organic systems, it is chemically inert over a relatively wide range of pH values; is white or near white in color; has good covering or hidding power when used as a pigment of extender in coating and filling applications; is soft and non-abrasive; has low conductivity values of both heat and electricity; and is lower in cost than most materials with which it competes. Some uses of kaolin require very rigid specifications including particle size, brightness, color, and viscosity. On the other hand some uses have no critical specifications, i. e. cement, where the only concern is light color and chemical composition. Ceramic specifications are variable in that each user may have slightly different requirement as to strength, pyrometric cone equivalent (PCE), plasticity, and color depending upon the body formulation. In general the value of a kaolin product is based upon color, brightness, and particle size with a white, bright, fine particle size kaolin having the highest value.

This paper will outline and discuss some of the basic tests for evaluating a kaolin deposit particularly for use in paper, paint, ceramics, rubber, plastics, and some other applications. The matter of drilling, sampling, and calculating reserves, which are very important, will not be discussed in this paper.

The following definition of kaolin is used in this paper: "kaolin is a clay consisting of substantially pure kaolinite, or related clay minerals, that is naturally or can be beneficiated to be white or nearly white; will fire white or nearly white; and is amenable to beneficiation by known methods to make it suitable for use in whiteware, paper, rubber, paint, and similar uses. The term is applied without direct relation to the purity of deposits. Many kaolins are sedimentary or secondary in origin and are very pure and required very little concentration of beneficiation in preparation for market. Many other kaolins are primary (hydrothermal or residual) in origin and contain as little as 10 percent kaolinite which requires considerable concentration and beneficiation to recover a marketable kaolin.

The largest single user of kaolin is the paper industry which accounts for almost 70 percent of the shipped tons in the United States and about 50 percent of the world tonnage. It is estimated that the world tonnage is approximately 17 million with 7 million being produced in the United States and 3.5 million in England. Thus it is evident that over half of the world's tonnage comes from two areas; Southeastern United States, i. e. Georgia and South Carolina, and Southwestern England — the Cornwall area.

Evaluation tests to determine the physical properties of kaolin are very important because different kaolin deposits can give such different test results. If one took a very fine particle size kaolin and a very coarse particle size kaolin and compared many of the physical properties the results would make one conclude that they were testing different minerals. There are many tests that are used to evaluate kaolin but only the more important will be discussed in this paper. The tests will be divided into sections, general evaluation, paper, ceramics, rubber, paint, and other uses.

GENERAL EVALUATION TESTS

In order to fully evaluate potential uses of kaolin many tests are necessary; however, a series of tests that will give a good indication of some of the more important physical properties and can be used as screening tests especially for coating, filling, and extender applications are as follows:

1. Mineralogy
2. Screen Residue (GRIT)
3. Particle size distribution
4. Brightness
5. Viscosity
6. pH

Mineralogy — The mineral content of a kaolin is very important in assessing the applications and the results of many tests for determining the physical properties and also for determining the beneficiation processes that may be needed to produce a saleable product. X-ray diffraction of the whole sample will give a quick assessment of the gross mineral gy but in many instances minor quantities of illite and smectite will not be detected. Separation of the 2 micron fraction and the 0.5 micron fraction and making oriented slides will enhance the basal reflections of the clay minerals and enables one to detect the presence of very small quantities of these layer silicates. The presence of quartz, cristobalite, alunite, smectite, illite, muscovite, biotite, chlorite, gibbsite, feldspar, anatase, pyrite, or halloysite certainly will effect the beneficiation steps and the possible uses of the kaolin. In many instances one cannot detect the presence of halloysite in the kaolin using X-ray diffraction techniques and so it is prudent to make some scanning electron micrographs and/or a differential thermal — thermal gravimetric analysis to detect either hydrated halloysite, alunite, gibbsite, or smectite. The presence of smectite and/or alunite in the kaolin causes high viscosities, halloysite also causes high viscosity and lowers the opacity of hiding power, and quartz and/or cristobalite in the finer particle sizes gives high abrasion values. X-ray diffraction can also be used to determine variations in kaolinite crystallinity which has a marked effect on physical properties [MURRAY and LYONS, 1956].

Screen Residue (Grit) — This test gives the percentage of particles that are retained on a 325 mesh screen (44 micron openings). Quartz, mica, and feldspar along with agglomerates of tightly bonded clay are the most common minerals retained on the screen. The percentage of the screen residue is important in determining the percent recovery of minus 44 micron material as it is this fraction that is the more important in either wet or dry processing plants. The procedure is described as method T681-SU-71, a standard procedure published by the Technical Association of the Pulp and Paper industry. The procedure involves weighing out a specified amount of kaolin, dispersing the kaolin in a measured amount of water, blunging the clay on a high speed mixer for a specified time, screening, drying, weighing, and determining the percentage of material retained on 325 mesh screen.

Particle Size Distribution — Particle size distribution is one of the more important properties of the kaolin as it effects viscosity, brightness, opacity, gloss, ceramic strengths and shrinkage, and many other properties. Sedimentation methods based upon Stoke's law are utilized for measuring particle size. The results are expressed in terms of "equivalent spherical diameter" (esd), the diameter of a sphere having the same specific gravity that settles at the same rate as the particle in question. Kaolin particles are platy or blocky, not spherical, but the results of a sedimentation analysis can be correlated with some physical properties relating to coating kaolins, filler and extender kaolins, and ceramic kaolins. Procedures limited to gravitational sedimentation are inaccurate for kaolin particles finer than 1 micron in e. s. d., and centrifugal procedures are used to determine the sizes below 1 micron e. s. d. Standard method T649-SU-68 of the Technical Association of the Pulp and Paper industry is the suggested method for determining the particle size distribution of kaolin. This TAPPI method outlines the procedure to follow, the apparatus needed, how to calculate e. s. d., and how to report the results.

Brightness — the brightness of kaolin is a most important physical property because it determines the potential uses and prices that can be charged. In general the higher the brightness of the kaolin the more valuable it is. Again the Technical Association of the Pulp and Paper industry has published a standard method T646-73 for measuring brightness. The standard brightness values are measured at 457 millimicrons and the standard (100%) against which the samples are compared is smoked magnesium oxide. The TAPPI method outlines the way in which the sample is to be prepared in order to achieve reproducible results and gives the type of instrumentation that is used to make the measurement at 457 millimicrons.

Viscosity — Flow properties of kaolin slurries are very important determinations because kaolin is used in slurry form in so many industrial application and particularly in two of the largest user industries, paper and paint. Again the Technical Association of the Pulp and Paper industry has published TAPPI method T648-SU-72 which describes the apparatus, calibration, who to report the results, and the precision of the test. Measurements of viscosity of the kaolin — water slurries are made at precise solids levels which is 70 percent for the sedimentaray kaolins of Georgia. Low viscosity clays are requried in the paper industry because the kaolin coating color must flow easily as it is applied to the paper sheet and not leave streaks and blotches which can be caused by high viscosity coating colors.

pH — The pH of untreated kaolin slurries normally ranges from 4.5 to 6.5. A high pH generally indicates the presence of soluble salts which if they are not removed, can cause severe problems in many applications. The technical Association of the Pulp and Paper industry has published TAPPI method T667-SU-75 which describes the determination of the hydrcgen-ion concentrates (pH).

EVALUATION TESTS FOR USE IN PAPER

The paper industry is by far the largest user of kaolin. Kaolin is used both as a filler in the sheet and as a coating ingredient on the surface of the sheet Many special tests have been designed to evaluate kaolin as a filler clay in paper and as a coating clay on the paper. Some of the more important tests are listed as follows and will be described briefly.

1. Percent recovery as coating clays
2. Rheology of medium and fine particle size fractions
3. Color improvement (chemical, flotation, magnetic)
4. Dispersability and Disintegration
5. Sheet properties
   a) brightness
   b) whiteness
   c) opacity
   d) gloss
   e) smoothness
   f) ink receptivity
   g) film strength
6. Adhesive demand

Percent recovery as coating clays — The most important size fraction of kaolins for producing a coating clay is that portion 2 microns and less. The major coating clay used for publication grade paper contains 80 percent of the particles finer than 2 microns and for cover stock, calendars, company reports, etc. requires a coating clay with 92 percent or more of the particles below 2 microns. Therefore it is necessary to make fractionations in the laboratory and calculate the percentage of particles less than 44 microns, less than 2 microns, and less than 0.5 microns. Screening and gravity settling is generally used to make the separations and the results are calculated as percent finer than 2 microns.

Rheology — Fluid dispersions are prepared at a given percent solids and low shear and high shear viscosity are measured. Low shear rheology seems to be controlled primarily by surface area, with viscosity increasing with decreasing particle size. High-shear rheology seems to be controlled largely by particle packing. *Fig. 1* shows the relationship between particle packing and viscosity. The dashed lines represent the effective volume of each particle. The right hand side of the diagram shows that high solids clay suspensions can be obtained most efficiently with random size distributions. *Fig. 2* shows the three types of viscous flow that are of particular interest in paper coating kaolins. Newtonian flow occurs when the viscosity remains constant as the shear rate is increased or decreased; thixotropy occurs when the viscosity decreases as the rate of shear is increased; and dilatancy occurs when the viscosity increases rapidly as the rate of shear increases. Measurements of viscosity of the clay-water slurries are made at precise solids levels, usually 70 percent for Georgia coating clays. Low shear viscosity is usually 30 centipoise or less at 20 revolutions per minute using a standard Brookfield viscosimeter, the standard unit used to measure low shear viscosity. High shear viscosity is measured using a Hercules viscometer [MURRAY, 1976].

Color improvement — Most kaolins require color beneficiation to get the maximum brightness and whiteness from the product. The most common method used to improve color is to chemically leach the soluble iron from the kaolin. The kaolin slurry is acidified, using sulfuric acid, to pH 3 and then a strong reducing agent sodium hydrosulfite is added (0.3 to 0.5 percent by weight equivalent of SO_2 on the weight

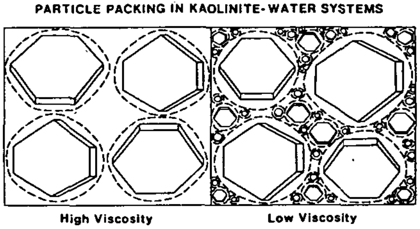

Fig. 1. Relationship between particle packing and viscosity

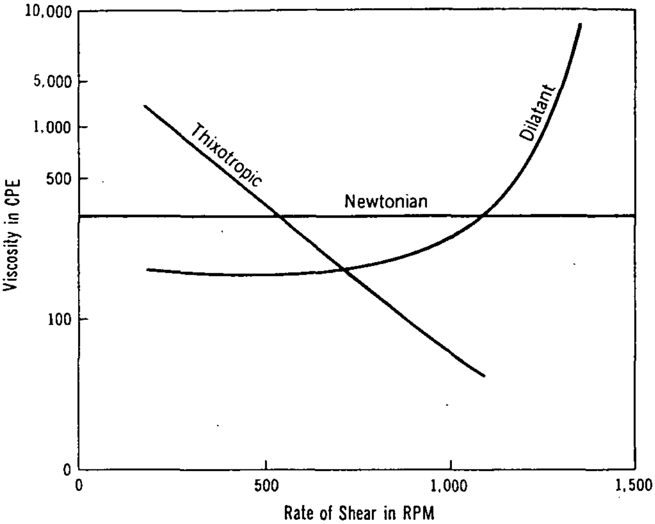

Fig. 2. Types of viscous flow

of dry clay) to reduce the iron to produce a soluble iron sulfate which is removed in the filtrate as the clay is dewatered by filtration. This leaching of soluble iron can significantly improve the color in many kaolins. High intensity magnetic separation will remove the iron and titanium minerals *(Fig. 3)* and produce a significant improvement in color [IANNICELLI, 1976]. Flotation also removes iron and titanium minerals and the resulting product is very white and bright [GREENE and DUKE, 1962].

Dispersability and disintegration — In order to achieve optimum results with a coating clay the kaolin particles must be completely dispersed. Many kaolins are easily dispersed using small amounts (0.2 to 0.5 percent) of alkali phosphates and silicates. In order to be utilized as a paper coating clay the kaolin must be able to be easily dispersed. Disintegration is a measure of the presence and amount of clay agglomerates in a coating clay. Aggregations of clay particles are caused during processing because of cementation or sintering and are difficult to disintegrate during normal makedown of the coating clay. The disintegration test consists of the application of a controlled amount of work which is sufficient to disperse the normal kaolin slurry. After this work is applied to the kaolin slurry, the slip is poured through a 325 mesh sieve and the agglomerates remain on the sieve and the amount can be determined.

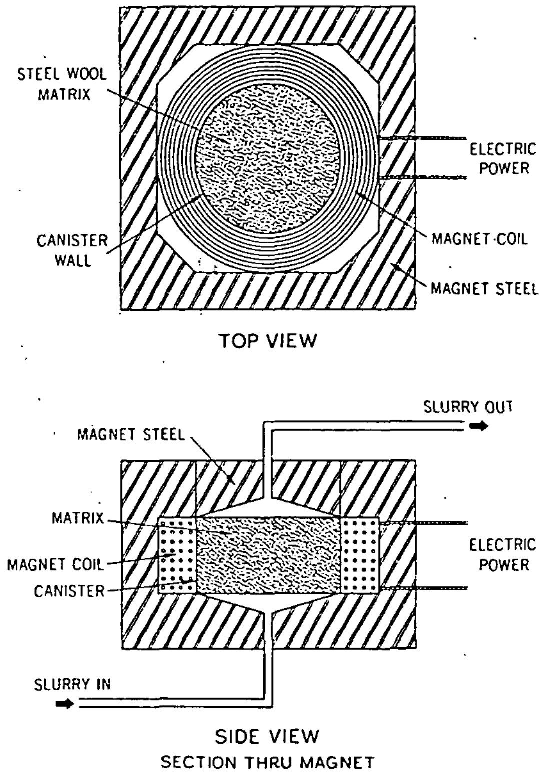

Fig. 3. Diagrammatic representation of high intensity magnetic separator

Sheet properties — Standard sheets of paper can be coated with a coating color consisting of kaolin and binder using standard procedures as outlined by the Technical Association of the Pulp and Paper industry. The coated sheet must be conditioned, calendared, dried and have a known amount of coating on the surface. Many properties can be measured and compared such as brightness, whiteness, opacity, gloss, smoothness, ink receptivity, and film strength. All these test procedures are available as TAPPI standards from the Technical Association of the Pulp and Paper industry [BRITT, 1970, p. 665]. These tests enable one to evaluate the properties of a particular clay for use for coating paper.

Adhesive demand — This is another standard test of the Technical Association of the Pulp and Paper industry. An adhesive such as starch or latex binds the kaolin particles together and to the sheet of paper. The adhesive is much more expensive than the clay so the minimum quantity that will give the necessary binding is used. A high surface area or fine particle size kaolin will require more binder than a coarse particle size kaolin. Measurement of the optimum amount of adhesive is necessary in order to get a coated surface that will not separate or pull away from the paper sheet during printing using tacky inks.

Abrasion — The hardness of particles other than kaolin in the clay can be a very important parameter because of marking on the sheet, wear on the coating applicators, and on the type used in printing. A standard test called the Valley abrasion test is available from the Technical Association of the Pulp and Paper industry. The test uses a slurry of kaolin and copper wire mesh. The kaolin slurry is circulated on the wire mesh and a micarta block is rubbed back and forth on the screen by a motorized arm for 600 cycles. The wear on the screen is measured by weight loss and is known as the abrasion value. The Georgia sedimentary kaolins have very low abrasion values.

EVALUATION TESTS FOR CERAMICS

The ceramic industry is a large user of kaolin clays in whitewares, sanitaryware, refractories, and insulators. Several tests are used to evaluate kaolins for use in ceramics. These will be described briefly.

1. Plasticity
2. Shrinkage
3. Modulus of Rupture
4. Absorption
5. PCE
6. Fired color
7. Casting rate
8. Chemical Analysis

Plasticity — Plasticity or workability is an important property and is a mesaure of the ease with which a body can be formed into various shapes. Plasticity can be measured using compression and/or tension tests which measure the resistance to deformation and the amount of deformation before cracking. The simplest analysis of plastic flow may be made from a stress strain diagram. Several tests have been designed to measure plasticity [Norton, 1970, p. 134].

Shrinkage — Ceramic articles undergo drying and firing shrinkage during the manufacturing sequence. Linear shrinkage, i. e. the amount by which each dimension changes, is more commonly reported than volume shrinkage. The simplest way to determine linear shrinkage is to make a measurement of the dimensions before and after the shrinkage occurs. Standard size bars can be made up and dried and fired to determine the linear shrinkage.

Modulus of Rupture — The modulus of rupture (MOR) is the fracture strength of a material under a bending load. The determination of the MOR is a simple measurement and is a standard quality control test. The MOR measurement is made on a long bar of either rectangular or circular cross section, supported near its ends, with a load applied to the central portion of the supported span. The American Society of Testing Materials has standard methods for testing MOR of various ceramic materials.

Absorption — Absorption is a measure of the porosity and is usually a very carefully controlled property. The greater the porosity, the more likely will be the penetration of liquids and vapors which may cause structural damage. The American Society of Testing materials has published a set of standard test methods for porosity and absorption of ceramics.

PCE — Pyrometric cone equivalent is a measure of the combined effects of temperature plus time during the firing operation. A standard series of pyrometric cones are formulated to provide end points corresponding to reproducible amounts of heat work. Pyrometric cones are used to test the vitrification point of clays. The clay material is molded into the standard cone shape and is heated along with a number of standard cones so that its end point can be determined in terms of an equivalent cone number. This number is known as the pyrometric cone equivalent of that particular clay (ASTM method C24-56).

Fired color — This test is simple in that a small bar or a plaque can be made up and fired so that the fired color can be determined.

Casting Rate — The casting rate can vary over a wide range depending on the slip composition and the wetness and age of the mold. A reasonably fast casting rate is desirable to permit a faster mold turnover. The viscosity and thixotropy of the slip are most important in determining casting rate.

Chemical Analysis — Chemical analysis of clays is sometimes important to know particularly the iron, alkalis, and alkaline earth elements along with the aluminum and silicon content. Many ceramic properties can be related to the chemical analysis such as refractoriness, casting rate, and fired color.

RUBBER TESTS

Kaolin is used in rubber because of its reinforcing and stiffening properties and because of its low cost. Fine particle size kaolins give good resistance to abrasion and are used extensively in non-black rubber goods. The kaolins that are used in rubber contain a maximum of 1% free moisture. Other tests that are important in evaluating kaolins for use in rubber are:

1. Water Settling Characteristics
2. Oil Absorption
3. Stress-Strain
4. Tear Resistance
5. Abrasion Resistance
6. Heat Generation
7. Energy rebound
8. Extrusion and Plasticity
9. Hardness
10. Aging Characteristics
11. Water absorption

These tests are all described in detail in the book entitled Kaolin Clays and Their Industrial Uses published by the J. M. Huber Corporation of Edison, New Jersey. All these tests have a particular value in relating to certain characteristics imparted to the rubber product. For example the Water settling test gives a good idea of the reinforcing characteristics of the clay and the Oil absorption also correlates with reinforcement. The other tests listed above are run on the rubber itself after filling with the clay and require specialized equipment.

PAINT TESTS

Kaolin clays are used extensively in paints particularly in water based paint systems. Kaolin is a functional extended pigment that has good covering or hidding power, imparts desirable flow properties to the paint, and is low in cost. Standard moisture and oil absorption tests are run on all paint clays along with more specialized tests. Low moisture of less than 1% is a requirement for paint clays and oil absorption relates to a parameter call vehicle demand in the paint. The test indicates surface area and absorption in the paint system. Other tests that are run on paint clays are:

1. resistivity
2. fineness of grind
3. performance tests

Resistivity — This test is to give an index of the amount of residual soluble salts in the clay. The higher resistivity values reflect a low soluble salt content. Depending on the paint system all clays that are used have a resistivity specification because a high soluble salt content adversely affects the dispersion of the ingredients in the paint and alters certain physical properties. The test requires a conductivity bridge to measure the conductivity.

Fineness of grind — This test measures the dispersion of the kaolin and highlights the fineness of the particles. A common measurement device is the Hegman gauge which is used extensively as a control device to measure the fineness of the kaolin product.

Performance tests — Actual paint formulations are made up with all the ingredients and many measurements such as gloss, color, smoothness, flow characteristics, dispersion, stability, weathering characteristics, aging, ank many other properties are determined.

MISCELLANEOUS TESTS

Kaolins are used for many industrial applications so there are other specific tests that may be required. These woud include such tests as bulk density, surface area, various special viscosity measurements, cation exchange capacity, and many others. These tests would be prescribed by the user.

CONCLUSIONS

Kaolins are tested initially for their mineral content, particle size, brightness and color, viscosity, and pH. These tests give a good indication of the potential applications. After these potential applications are determined then evaluation for paper, paint, ceramics, plastics, rubber, and others can be made. For example if the initial evaluation indicates high viscosity then the kaolin could not be used for paper coating but if the brightness and color were good it coud be used for filling applications and perhaps ceramics. Because there are so many industrial uses for kaolin, one bad characteristic such as viscosity does not mean that it would not be a very good ceramic clay. Tests must be done, however, in order to establish its ultimate utilization.

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