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A study of Missouri Flint Clay

Edmond Preston Hyatt

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A STUDY OF MISSOURI FLINT CLAY

BY

EDMOND PRESTON HYATT

A

THESIS

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Professor of Ceramic Engineering

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A STUDY OF MISSOURI FLINT CLAY

I. Introduction

The Problem

The problem is one of attempting to explain the peculiar nature of Missouri Flint Clay and to expand the knowledge concerning it. Among the questions for which answers are sought are: What makes Missouri Flint Clay so hard? What happens to Missouri Flint Clay when it is ground? What is the mineralogical constitution of Missouri Flint Clay?

How much (or little) is known about Missouri Flint Clay may be seen in the Review of Literature, pp. 2-9.

Importance of Missouri Flint Clay

The Missouri refractory industry took a new turn soon after 1910 when the north-central Missouri Fire Clays were developed. These clays besides the valuable diaspore and burley types grade from flint to plastic fire clays. The flint clay is utilized for the high refractoriness it imparts to mixtures with plastic clay.

Relationship of Problem to Refractory Industry

The problem has more than mere academic interest and potentially the information on the composition of flint clay could afford important economic improvements. It is not beyond reason to suppose that the industry may be able to improve usage of flint clays or provide substitutes having as good, if not better, properties than obtained at present from the flint clays.

II. Review of Literature:

A. Nature of Missouri Flint Clay:

Differentiating Characteristics

The name "Flint" as applied to the clay under discussion has no connection whatever to the variety of the mineral, quartz, called "flint". It is the typical conchoidal fracture of flint which is responsible for the association of the name in "Flint Clay".

Norton(1) describes flint clay as being "compressed into a hard, rocklike mass and (which)requires fine grinding to develop plasticity;.....". Plastic clays, in contrast, "are soft and easily tempered into a plastic mass...".

What Makes Flint Clay Hard?

In 1921(2) the statement was made, in reference to soils, that "ultra" clay was the principle binding material . "Ultra Clay" is identified as, "hydrated silicate of alumina, silicic acid, organic matter or possibly $Al(OH)_3$".

Stull and Bole(3) in 1926 declare that the hardness of clays is due to free silicic acid present and that all clays

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(1) F. H. Norton, Refractories, N. Y., McGraw-Hill Book Col, 1942. p. 147.

(2) Moore, Fry, and Middleton, Methods for Determining the Amount of Colloidal Material in Soils, J. Ind. and Engr. Chem. Vol. 13, 1921, p. 527.

(3) R. T. Stull and G. A. Bole, Beneficiation and Utilization of Georgia Clays. U. S. Bur. of Mines Bulletin 252, 1926.

were "hard" when laid down. "Soft" clays result when the silicic acid has been removed. Flint clays may result where there was some addition of silicic acid to the original hard clay.

Allen(4) believes that diaspore ($Al_2O_3 \cdot H_2O$) results from desilication of flints and other clays, thereby inferring that the bonding agent is silicic acid.

Dr. W. D. Keller, professor of Geology at the University of Missouri and a leading clay mineralogist, stated as late as September 1949 that, "We do not know what makes Missouri flint clay so hard....it's either silica or alumina gels".(5)

Mineralogy of Missouri Flint Clay

Halloysite was termed the principle mineral occurring in sink-hole deposits of flint clay as early as 1934(6) and as recent as 1943(7); in 1936(8) kaolinite was reported as

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(4) Victor T. Allen, Mineralogical Composition and Origin of Missouri Flint and Diaspore Clays, Appendix IV, 58th Biennial Report, Missouri Geological Survey and Water Resources, Rolla, Mo. p. 14, 1935.

(5) Private conversation with the author, 17 Sept., 1949.

(6) C. S. Ross and P. F. Kerr, Halloysite and Allophane, Prof. paper 185 G, U. S. Geological Survey, pp. 135-148, 1934.

(7) H. S. McQueen and P. G. Herold, Fireclay Districts of East Central Missouri, Missouri Geol. Sur. and Water Resources, Vol. XXVIII, 2nd Series, 1943, p. 243.

(8) R. E. Grim and R. H. Bray, The Mineral Constitution of Various Ceramic Clays, Jour. Amer. Cer. Soc., Vol. 19, November 1936, p. 310.

principle mineral.

The various opinions are stated as follows:

Ross and Kerr(6) identified the halloysite by X-ray diffraction and Allen(8a) by petrographic microscope. That halloysite was present in large amount was "confirmed" by X-ray patterns which also indicated micaceous flakes of kaolinite, up to 40%. The conclusion was that flint clays were a mixture of halloysite, kaolinite, and quartz with some minor minerals.

Also by the petrographic method Herold(7) reported that typical flint clays are chiefly halloysite with some limonite stained clay. Kaolinite may be present in small amount but there is generally very little in the way of accessory minerals.

Grim(8) reported that he could find no halloysite in his samples of Missouri flint clay but did identify kaolinite. He also claims to have found 15 - 25% boehmite ($Al_2O_3 \cdot H_2O$) in the coarse (+1.0 micron) fraction and less than 5% of a sericite-like mineral in the 0.1 to .06 micron fraction.

Petrographically these minerals have the following properties(9, 10):

(8a) Allen, Op. Cit., p. 7.

(9) A. F. Rogers and P. F. Kerr, Optical Mineralogy, McGraw-Hill Book Co., N. Y., 1942.

(10) Other diagnostic properties of kaolinite, halloysite, and other clay minerals are incorporated hereinafter under the appropriate section.

Name	Kaolinite	Halloysite	Diaspore
composition	$Al_2O_3 2SiO_2 2H_2O$	$Al_2O_3 2\pm SiO_2 2\pm H_2O$	$Al_2O_3 \cdot H_2O$
n_α	1.561	n = 1.549-561	1.702
n_β	1.565		1.722
n_γ	1.566		1.750
$n_\gamma - n_\alpha$	.005	.001	0.048
2V	variable		84°
(+) or (-)	(-)		(+)

Boehmite is dimorphous with diaspore.

Ross(11) gives for kaolinite $n_\alpha = 1.560$, $n_\gamma = 1.566$ and the crystal habit as plates forming curved groups; extinction is parallel; halloysite has conchoidal fracture; n = 1.552 and is isotropic. He further states that optical properties of halloysite are not conclusive and X-rays must be relied upon.

For halloysite with no diaspore and low alkali, Allen(8a) gives n = 1.563 - 1.567 which may account for the difference in identification of kaolinite and halloysite.

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(11) Clarence S. Ross (Chief of the Section of Petrology, USGS), Minerals and Mineralogical Relationships of the Clay Minerals, Jour. Amer. Cer. Soc., Vol. 28, p. 173, 1945.

Chemistry of Missouri Flint Clay

	Missouri(13) Flint Clay	Average(14) for Mo. Flint	Halloysite(12) $Al_2O_3 2SiO_2 3H_2O$	Kaolinite(12) $Al_2O_3 2SiO_2 2H_2O$
Al_2O_3	39.35	38	36.9	39.5
SiO_2	43.32	43	43.5	46.5
LOI	13.86	13	19.6	14.0
Fe_2O_3	.77	small		
TiO_2	2.00	"		
CaO	.16	"		
MgO	.33	"		
Alkalis	.22	"		

	Missouri(12,13) Plastic	Burley(12,13) Flint	Kentucky(12,15) Flint
Al_2O_3	31.16	48.03	39.60
SiO_2	53.12	34.62	42.76
LOI	11.26	13.30	13.78
Fe_2O_3	1.18	1.09	.96
TiO_2	1.76	2.28	.80
CaO	.12	.25	.12
MgO	.48	.56	tr
Alkalis	.49	.44	.70

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(12) For the purpose of comparison.

(13) M. C. Booze, The Chemical and Physical Properties of Fire Clays from Various Producing Districts, Jour. Amer. Cer. Soc., Vol. 8, p. 655, 1925.

(14) McQueen, Op. Citl, p. 154.

(15) H. D. Easton, Report on the Technology of Kentucky Clays, Kentucky Geological Survey, Series IV, Vol. I, Part II, p. 766.

Marshall has made an important contribution on the relationship of the chemical analysis to structure in which he indicates that structurally kaolin may be written as, $Al_2O(OH)_4Si_2O_3$ and the ratio of the oxides may vary as, alumina : silica :: 1 : 1.85 to 1 : 2.94. Similarly, halloysite, $Al_2(OH)_6Si_2O_3(OH)_2$, has an oxide ratio of 1 : 1.65 to 1 : 2.06 (16).

Ceramic Properties of Missouri Flint Clay

The following firing properties of Missouri flint and other clays are more or less typical:(17)

Property	Flint	Plastic	Burley
PCE	32-33	31	33-36
Water of Plasticity %	23	35	30
Drying Shrinkage	6	12	8
Firing shrinkage Cone 14	10	6	5
Absorption-cone 14	7	3	22

High fusion point and attendant low re-heat shrinkage are chief factors influencing the use of Missouri flint clay in the ceramic industry.

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(16) C. E. Marshall, Chemical Constitution as related to the Physical Properties of the Clays, Trans. Brit. Cer. Soc., Vol. XXV, p. 401, 1936.

(17) McQueen, Op. Cit., pp. 216-244.

B. Origin of Missouri Flint Clay (18, 19, 20, 20a)

The flint clay in Missouri is usually found in pockets, basins and irregularly shaped bodies which have the earmarks of sink holes. The distinctive diaspore pit is the extreme case which is lined with sand then filled successively with plastic, semi-flint, flint, burley, and diaspore layers. Many such deposits contain nothing more important than flint clays though the features of formation are thought to be similar to the diaspore pit.

Allen(18) describes how these deposits were made as follows: The surface was originally a low, gently undulating plateau with numerous irregularities. The climate was warm and moist, typical of Pennsylvanian time. The dolomitic limestones were slowly dissolved leaving thick residual soil of quartz, halloysite, kaolinite, and some other minerals. These were deposited with sand on bottom, sandy clay and then clay. The bedding of sand in depressions conformed to the slope and it was blanketed by a thick layer of clay. Some of the depressions were not disturbed though there was some localized drainage so solution of underlying dolomite was greatest below the deposit of clay.

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(18) Allen, Op. Cit., p. 15.

(19) H. S. McQueen, Geologic Relations of the Diaspore and Flint Fire Clays of Missouri, Jour. Amer. Cer. Soc., Vol. 12, p. 687-697, 1929.

(20) M. H. Thornberry, A Treatise on Missouri Clays, Bulletin, University of Missouri, Sch. of Mines and Met., Vol. 8, p. 9-69, 1925.

(20a) H. A. Wheeler, Clay Deposits, Missouri Geological Survey, Vol. XI, pp. 201-240, 1896.

Slumping occurred as solution continued. The flint clay fractured as the beds slumped into the sink holes and the solutions traveled along these fractures and altered the flint clay to burley and to diaspore clay.

The carbonate solutions thought to be present in these waters (H_2CO_3, alkaline carbonates, or magnesium acid carbonate) have been proved capable of removing colloidal silica.

Typical clay pits near Rolla, Missouri, are described by Wysor(21) as follows:

The average diameters are about 125 feet though the range is about 75-250 feet. The depth may vary from 10 to 150 feet with an average of about 25 feet. About 15,000 tons may be taken from such a pit divided into the following proportions: smooth flint and plastic clay, 8,000 T.; No. 3 grade diaspore (55% Al_2O_3), No. 2 Diaspore (60% Al_2O_3), and No. 1 diaspore (65% Al_2O_3), 4,000 T., 2,000 T., and 750 T., respectively. The abrasive grade diaspore (70% Al_2O_3) may be present in amount of 250 T.

Other pits contain largely flint and plastic flint clays.

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(21) D. C. Wysor, Diaspore Clay of Arkansas and Missouri, Jour. Amer. Cer. Soc., Vol. 6, pp. 501-509, 1923.

C. Research Methods and Procedures as Applied to Similar Problems:

1. Mechanical Analysis(22)

General

The separation of differently sized particles for examination or measurement is termed mechanical analysis and may take the form of screening (or sieving), elutriation, air separation, centrifuging, sedimentation or any combination of these.(23)

The only methods having important application to clay particles in the range of this study are those involving sedimentation and centrifuging or other means utilizing Stokes' Law (q. v., p. 11) where the small particles settle out in a liquid medium. This grouping is suggested for sub-sieve grain sizes common in clays.(24)

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(22) W. C. Krumbein, A History of the Principles and Methods of Mechanical Analysis, Jour. Sed. Petrology, Vol. 2, pp. 89-124, 1932.

(23) A. B. Searle, The Chemistry and Physics of Clays and other Ceramic Materials, London. Ernest Benn Limited, 1933, p. 55.

(24) G. A. Loomis, Grain Size of Whiteware Clays as Determined by the Andreasen Pipette, Jour. Amer. Cer. Soc., Vol. 21, p. 393-399, 1938.

Stokes' Law(25)

The rate at which particles will settle in a fluid medium was evaluated by Stokes in 1845 and his statement of the principles involved has become known as Stokes' Law. It is tersely stated by the equation,

$$V = \frac{2(D-d)}{9\eta} \quad g\ r^2 = \frac{h}{T}$$

where V = velocity of particles (cm/min)
η = viscosity of the liquid (poises or dyne-cm /sec^2)
r = radius of particles (cm)
g = gravitational constant (980 cm/sec^2)
d = density of liquid (gm/cc)
D = density of particles (gm/cc)
h = height of fall (cm)
T = time of fall (sec)

The following assumptions must be made to render this equation valid:

(a) Particles of solid matter are much larger than those of the liquid. Casagrande (26) says the limit of Stokes' law is between 0.2 to 0.0002mm.

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(25) Searle, Op. Cit., pp. 66-68.

(26) Arthur Casagrande, Die Aräometer Methode zur Bestimmung der Kornverteilung von Böden, Berlin, 1934.

(b) Liquid is homogeneous and infinite compared to the particles. A one per cent concentration is the theoretical limit though up to 5% is used.

(c) The particles are smooth, rigid spheres.

(d) There is no slipping between particles and liquid.

(e) Velocity is small.

(f) Particles are small.

(g) Particles are free to fall.

(h) Temperature remains constant.

(i) There are no currents in the medium.

Measurement of variations of Hydrostatic Pressure

Kelly in 1924 proposed measurement of particle sizes by change in the hydrostatic pressure at a given level as particles settle out of the suspension. Calculations of sizes of particles settled out are based on Stokes' law and it is possible to relate the pressure (due to particles still in suspension) to the particle size and time.(27)

Several modifications have been made to this type of apparatus, one of the latest being the Dotts' tube.(28)

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(27) W. J. Kelly, Determination of Distribution of Particle Size, Ind. Eng. Chem., Vol. 16, p. 928, 1924.

(28) Walter M. Dotts, Measuring the Distribution of Particle Size in Dispersed Systems, Ind. Eng. Chem. Anal. Ed., Vol. 18, pp. 326-328, 1946.

One application was reported in the mechanical analysis of Portland cement though it is doubtful if this is being used extensively at present.(29)

The tubes consist essentially of a sedimentation chamber on the order of 2 cm diameter and a manometer tube connected at a height of about 20 cm.

There are several objections to this method and they limit application considerably:(30)

(a) Too difficult to start run with absolute homogeniety because coarse particles settle rapidly while filling tube.

(b) Suspension diffuses into the side (manometer) tube.

(c) Temperature changes affect readings greatly.

<u>Measurement of Change of Weight of Immersed Body</u>

This method is essentially one of obtaining the effect of change in density in the suspension but by using an object suspended in the liquid from a balance. Similar to this method is,

<u>Measurement of Change in Weight of Sediment Deposited</u>

Oden(31) and Svedberg(32) made great contributions to

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(29) Chas. G. Duncombe and Jas. R. Withrow, The Kelly Tube and the Sedimentation of Portland Cement, Jour. Phy. Chem., Vol. 36, p. 31, 1932.

(30) Loomis, Op. Cit., p. 396.

(31) S. Oden, The Size Distribution of Particles in Soils and Experimental Methods of Obtaining Them, Soil Science, Vol. 19, 1925.

(32) T. Svedberg, Colloid Chemistry, A. C. S. Monograph, N.Y., Reinhold Publishing Corp., p. 167-79, 1924.

the theory and practice of mechanical analysis in work largely on this type of apparatus. Oden developed an automatically recording device which used a self-balancing analytical balance, one arm of which was suspended with its pan in the sedimentation tube. The weight collected on the pan is recorded automatically on photographic film.

Centrifugal Force Methods

For the larger particles (over 2 microns) the sedimentation time is short enough under the force of gravity to permit rapid determination of particle sizes; but when the particles are smaller than two microns the tests require many days. Several methods are available to increase the force on the particles hence effectively increasing the gravity. Norton and Speil(33) recommend a long arm centrifuge which they say gives good results down to 0.05u. They actually measure the density of clay in suspension for given time it is under the given gravitational force (see next section for actual measurement).

Sharples(34) describes a centrifuge used to make

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(33) F. H. Norton and S. Speil, Measurement of Particle Sizes, Jour. Amer. Cer. Soc., Vol. 21, pp. 367-370., 1938.

(34) L. P. Sharples, Centrifugals as Applied to Colloids, in J. Alexander, Colloid Chemistry, Vol. 16, Reinhold Publishing Corp, N.Y., p. 800, 1946.

particle size separations after which the suspensoids are weighed dry to give the mechanical analysis.(35)

Marshall(36,37) further modified the centrifuge method by using a layer of high viscosity liquid on top of water.

Measurement of Variations of Density

While all methods mentioned thus far are essentially measurements of change in density as particles settle out some have been developed which measure the density in a more conventional and direct manner. The Casagrande hydrometer(38,39) is a specially constructed hydrometer with a long thin stem. Density readings are taken at definite time intervals and these densities are related to weights

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(35) Moore, Fry, and Middleton, Op. Cit., p. 527.

(36) C. E. Marshall, Clays as Minerals and as Colloids, Trans. Eng. Cer. Soc., Vol. 30, pp. 81-97, 1931.

(37) C. E. Marshall, Studies in the Degree of Dispersion of the Clays, I. Notes on the Technique and Accuracy of Mechanical Analysis Using the Centrifuge., Jour. Soc. Chem. Ind., Vol. 50, p. 444, 1931.

(38) A. Casagrande, Op. Cit.

(39) Arthur Casagrande, Hydrometer Method of Mechanical Analysis of Soils and Other Granular Materials, Blue-printed bulletin, Mass. Inst. of Tech., 1931.

of particles not settled out of suspension. Complicated calculations render use of a nomograph developed by Casagrande advisable. The serious objection to this method lies in the fact that the hydrometer must be immersed in the suspension for each reading which causes error due to agitation.

The density of a weak suspension can be determined by measurement of the light transmitted through a sample at given height and time. Such an apparatus (Wagner Turbidimeter) is widely used in the Portland Cement industry.(40)

Another method of density determination was developed by Andreasen and is the standard method in many laboratories(41). Small pipette aliquots are taken at definite time intervals and fixed heights. The samples are dried and the actual weight of clay in aliquot is found. This shows the weight of particles not settled out and which are, then, smaller than those particles which have settled out. Loomis(42) and Krumbein(43) have made extensive comparisons

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(40) L. A. Wagner, Rapid Method for Determination of Specific Surface of Portland Cement, Proc. Amer. Soc. Testing Mat., Vol. 33, Part II, pp. 553-70, 1933.

(41) L. B. Olmstead, A Pipette Method of Mechanical Analysis of Soils Based on Improved Dispersion Procedure, U. S. D. A., Tech. Bul. 170, 1930.

(42) Loomis, Op. Cit.

(43) Krumbein, Op. Cit.

of all systems of mechanical analysis and both agree that the pipette method is best. Krumbein reported checks using this system of 1%.

Preparation of Samples for Mechanical Analysis

The mechanical analysis determines the distribution of sizes of individual particles in a sample hence preparation of agglomerate-free samples is essential. Preparation then is a problem of deflocculation.

The first step suggested by Olmstead(44) is to remove all organic matter with hydrogen peroxide; soluble matter is removed by filtration and washing. Deflocculation may be obtained with sodium oxalate, sodium pyrophosphate(45), ammonium hydroxide(46) or other suitable deflocculants. The ammonium hydroxide has the advantage of leaving no residue in the dried sample if such were to be taken.

Some investigators recommend dialysis for removal of adsorbed ions, but this requires much time and is termed unnecessary by most. Washing with distilled water will usually suffice. Electrodialysis has been known to cause decomposition of clay crystals and this objection would

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(44) Olmstead, Op. Cit.

(45) Loomis, Op. Cit.

(46) R. E. Grim, and W. F. Bradley, Investigation of the Effect of Heat on Clay Minerals, Illite and Montmorillonite, Report of Investigations No. 66, Ill. State Geol. Sur., p. 6, 1940.

indicate its non-use.

Agitation follows addition of chemical to complete the deflocculation.

Dilution to no more than 5% solids is necessary if interference of falling particles is to be eliminated.(47)

Fractionation of Clays

The separation of clay samples into fractions of definite size range has aided the study of clay mineralogy. It has been found that different clay minerals are more likely to be in one size range than in another, hence the fractions often separate distinct minerals.

In Marshall's important review of centrifugal methods of mechanical analysis(48) fractions were studied in the range of 0.05 to 2.0 microns. He proved that his fractions were correctly sized. The mineral Bentonite (montmorillonite), for example, fell in the range of -0.5 microns.

Kelley(49) concurred with most of Marshall's work and said montmorillonite was present chiefly in the range of -0.3 microns and that these lattice layers rarely exceed 1 micron while kaolinite is much larger.

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(47) Searle, Op. Cit., p. 67.

(48) C. E. Marshall, Studies in the Degree of Dispersion of the Clays, I. Notes on the Technique and Accuracy of Mechanical Analysis using the Centrifuge., Jour. Soc. Chem. Ind., Vol. 50, p. 444, 1931.

(49) Walter P. Kelley, Cation Exchange in Soils, Amer. Chem. Soc., Monograph No. 109, Reinhold Pub. Corp., N.Y., pp. 116-117, 1948.

Norton and Speil(50) also have done much work on fractionation of clay samples into "monodispersed systems".

Grim and Bray(51) divided clay into the following fractions: Superfine colloid, -.06u; fine colloid, 0.1 - -0.06u; coarse colloid, 1 - 0.1u; and residue, +1u. They found that for Phelps County, Missouri, flint clay that kaolinite (over 40%) and boehmite (15-25%) were present in residue; kaolinite alone was in the coarse colloid fraction while kaolinite and a "sercite-like" mineral were present in the fine fraction. They reported "little below .1 micron".

Effect of Grinding and Particle Size

The only known reference to the affect of grinding is reported by Laws and Page who dry ground kaolin for long periods of time and found that the effective particle size increased with grinding up to 96 hours and then decreased. They attributed this to a rearrangement of the crystal structure of the kaolinite.(52)

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(50) F. H. Norton and S. Speil, Fractionation of Clay into Closely Monodispersed Systems, Jour. Amer. Cer. Soc., Vol. 21, pp. 367-70, 1938.

(51) R. E. Grim and R. H. Bray, The Mineral Constitution of various Ceramic Clays, Jour. Amer. Cer. Soc., Vol. 19, pp. 307-315, 1936.

(52) W. D. Laws and J. B. Page, Changes Produced in Kaolinite by Dry Grinding, Soil Science, Vol. 62, pp. 319-336, 1946.

Surface Factor and Particle Size(53)

The mechanical analysis is usually reported as the weight (or %) of the total clay sample which is finer than a certain size. This is usually plotted on a graph in which the particle sizes are shown on a log scale and the % finer on a linear scale.

Since surfaces represent the most important aspects of particle sizes it is convenient at times to express the particle sizes, collectively for a sample, as a function of the surface represented. This is done as follows: first of all, the particles are assumed to be spheres (hence, for clays the term, 'equivalent spherical diameter', has important meaning); surface area for any one fraction =

$$\frac{\text{weight/fraction X Surface area/particle}}{\text{weight/particle}}\ ;$$

total surface factor is a summation of the surfaces of the fractions.

To determine the above it is necessary to find an average diameter which would aid in determination of the volume, surface area and weight. For want of contrary evidence the mathematical average diameter is used and this becomes,

$$\sqrt[3]{\frac{(d + d_s)\ \ (d^2 + d_s^2)}{4}}$$

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(53) A. I. Andrews, Ceramic Tests and Calculations, John Wiley and Sons, N. Y., pp. 119-123, 1928.

Where d = the larger diameter of the fraction and d_s = the smaller.

The weight per particle (W) equals the volume $(1/6 \pi d^3)$ times the density (S) of the material or, $W = \frac{S \pi d^3}{6}$, where d = average diameter of the fraction.

Surface area per particle = πd^2; weight per fraction equals W'; therefore the Total surface equals, $\frac{6W'}{Sd}$; the total surface for several fractions = $\frac{6}{S} \left(\frac{W'}{d_1} + \frac{W''}{d_2} + \frac{W'''}{d_3} \ldots\right)$ where $W' + W'' + W''' \ldots = 1$.

Relationship of Grain Size and Plasticity

That grain size has an important effect on plasticity and other 'ceramic' properties has been well shown by Whittaker(54). Among the relationships are the following:

(a) Plasticity is directly related to the surface area, hence, inversely to the particle size. Whittaker found that relative plasticity was higher for each successively smaller clay fraction studied.

Plasticity in this case was taken as the product of yield and strain.

(b) Plasticity is due to colloidal size particles in the system. He observed that kaolinite will be plastic only where the surface area is greater than 180×10^4 cm^2/100 gm. (a mean diameter of about 4 microns).

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(54) H. Whittaker, Effect of Particle size or Plasticity of Kaolinite, Jour. Amer. Cer. Soc., Vol. 22, pp. 16-23, 1939.

(c) Plasticity also depends upon size of the water film surrounding particles. That thickness for optimum plasticity is about 90 Å (0.09 microns).

(d) Fine grained (plastic) clays tend to have high drying shrinkage and,

(e) They generally have high dry strength.

Particle size itself is not, however, the only factor upon which plasticity depends because the above rules do not hold true in all cases; for instance, calcined plastic clays are not plastic after the heat treatment though the particles have not increased in size.(55)

2. Chemical Analysis(56)

Chemical analyses of clays are valuable for the information provided as to proportion of elements or oxides present; and presence of deleterious impurities. It is difficult to predict fusability, shrinkage, strength and other properties on basis of chemical analysis though often such a test reveals data of value(57).

The method of making chemical analyses for such material as flint clay is covered in publications of the ASTM(58) and will not be repeated here.

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(55) Searle, Op. Cit., p. 280.

(56) See page 6 for typical chemical analyses of flint and other clays as reported in the literature.

(57) Searle, Op. Cit., pp. 400-402.

(58) American Society for Testing Materials, Manual of ASTM Standards on Refractory Materials, Phila., Pa., pp. 101-104, 1948.

3. Differential Thermal Analysis

General Principles and Significance(59, 60, 61)

Studies of the heating characteristics of clay and various other minerals reveal that there are energy changes within the minerals which vary according to the temperature to which they are heated.

On Figure 1, page 24, is a manifestation of these energy changes as a sample of china clay (kaolinite) is heated uniformly. The change in temperature is not linear but is dependent upon certain conversions or inversions within the crystal structure of the minerals present in the sample.

The term 'differential thermal' refers to the technique involved in which a thermally inert substance is heated next to the mineral being analyzed. Where the energy changes occur within the mineral it will have a higher or a lower temperature than the inert substance, a thermal difference, hence, 'differential thermal' analysis.

When the temperature of the mineral being analyzed becomes lower than the inert substance, as the furnace is being heated, one concludes that an endothermic reaction is taking place; for a higher temperature it is an exothermic reaction.

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(59) R. E. Grim and R. A. Rowland, Differential Thermal Analysis of Clays and Shales, A Control and Prospecting Method, Jour. Amer. Cer. Soc., Vol. 27, 1944.

(60) Sidney Speil, Application of Thermal Analysis to Clays and Aluminous Minerals, U. S. Bur. Min., R. I. 3764, pp. 4-9, 1944.

(61) Norton, Op. Cit., pp. 137-139.

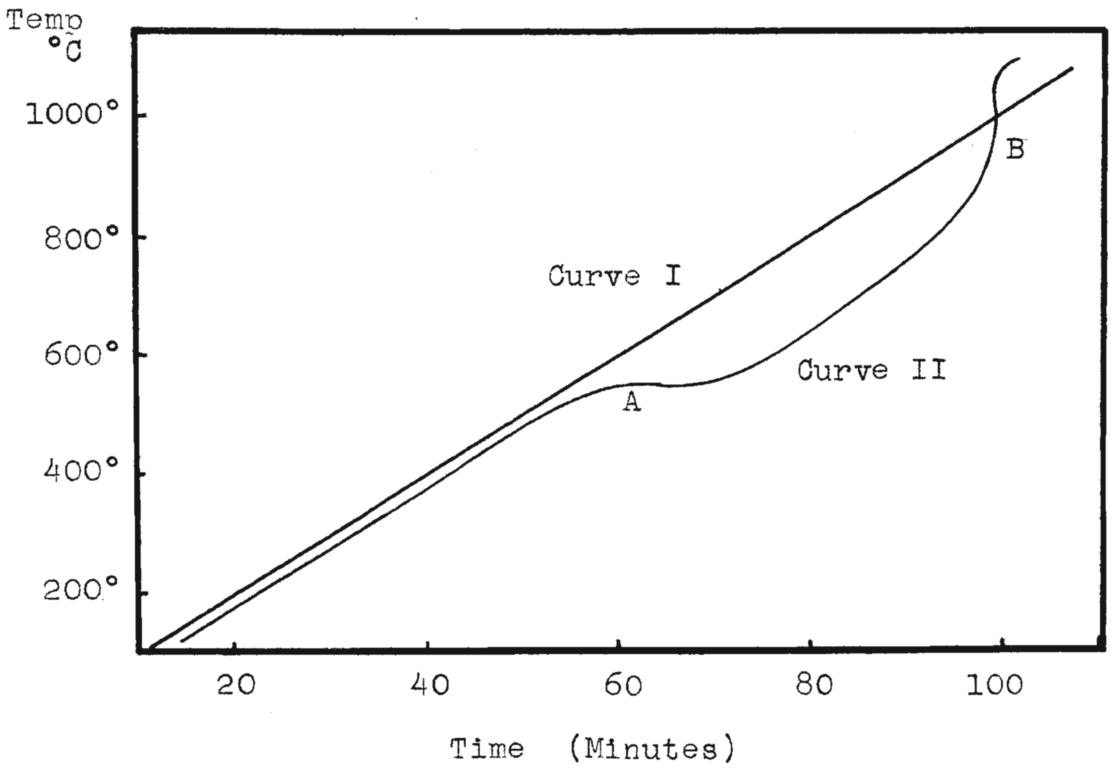

Fig. 1. Heating Curve for a Typical Kaolin.

Curve I : The heating curve for the furnace showing steady heating of 10°C per hour.

Curve II : The actual heating curve of the Kaolin showing a lag wherein the sample is cooler than the furnace. A greater cooling is shown for the region at A and a heating is shown for B.(61a)

(61a) Adopted from Searle, Op. Cit., p. 388 and H. Wilson, Ceramics-Clay Technology, N. Y., McGraw-Hill Book Co., 1927, p. 142.

The typical endothermic reaction (where energy is required) is one involving removal of water from crystal lattices. Exothermic reactions (where energy is given up) occur when carbonaceous substances are oxidized and where certain, not well explained, crystallographic changes take place.

Clay minerals (also many other substances) have their own distinct and endo- and exo-thermic reactions which are characteristic for each mineral species. For example, kaolinite has a definite endothermic reaction around 610° C. and an exothermic reaction at about 980° C.; halloysite, endothermic at below 150° C. and 490-560° C. and an exothermic at 880-930° C.(62) (Various investigators give slightly different temperatures.)

These typical clay reactions are thought to be, first, (endothermic) removal of water (OH) from crystals and then (exothermic) either the break-up into constituent oxides of anhydrous aluminosilicates or amorphous alumina to gamma alumina.(63,64)

Investigators make wide use of the characteristic reactions to qualitatively determine mineral constitution of various clays. Direct comparison is made between a known

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(62) Searle, Op. Cit., p. 391.

(63) Searle, Op. Cit., p. 390.

(64) Norton, Op. Cit., p. 283.

pattern of reactions and the unknown. (See also use of system with mixtures, pages 27 and 29).

Speil(65) points out that comparisons are justified for any mineral, such as kaolinite, "only when the standard mineral approximates the physical condition in which that mineral is present in the specimen being studied."

Apparatus and Equipment for Differential Thermal Analysis

Several detailed descriptions are available in the literature(66, 67, 68, 69) and will not be repeated here.

The essential features, however, are:

(a) Furnace whose temperature rise may be accurately controlled at, for example, 12 or 15° C. per minute.

(b) Instrument for measurement of temperature of furnace.

(c) Cup holders for both sample and inert material.

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(65) Speil, Op. Cit., p. 23.

(66) F. H. Norton, Critical Study of Differential Thermal Method for the Identification of the Clay Minerals, Jour. Amer. Cer. Soc., Vol. 22, pp. 54-63, 1939.

(67) L. H. Berkelhamer, An Apparatus for Differential Thermal Analysis, U. S. Bur. Min. R. I. 3762 (also Tech. Pap. 664) 1944.

(68) P. G. Herold and T. J. Planje, Modified Differential Thermal Analysis Apparatus, Jour, Amer. Cer. Soc., Vol. 31, pp. 20-22, 1948.

(69) R. E. Grim and R. A. Rowland, Op. Cit., pp. 6-9.

(d) Thermocouple junctions in both cups with leads of one metal and joining wire of the other metal.

(e) Galvanometer to measure current in differential thermocouple.

Differential Thermal Analysis of Pure Substances

Fig. 2, page 28, is a graphical representation of results of differential thermal analysis using fairly pure or representative substances.

Norton(70) and Speil(71) list the following as principle peaks for certain clay and other minerals:

	(70)	(71)
Kaolinite	610°	610°, 980°
Halloysite	310°, 575°	150°, 590°, 980°
Montmorillonite	875°	100-300°, 700°, 840 to 930°, 1050° (variable)
Diaspore	550°	550-580°
Gibbsite	360°	365°
Quartz		578°

Differential Thermal Analysis of Clays

Clays are composed of various clay and accessory minerals and their differential thermal curves are algebraic

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(70) F. H. Norton, Critical Study of Differential Thermal Method for the Identification of the Clay Minerals, Jour. Amer. Cer. Soc., Vol. 22, pp. 54-63, 1939.

(71) Speil, Op. Cit., p. 20.

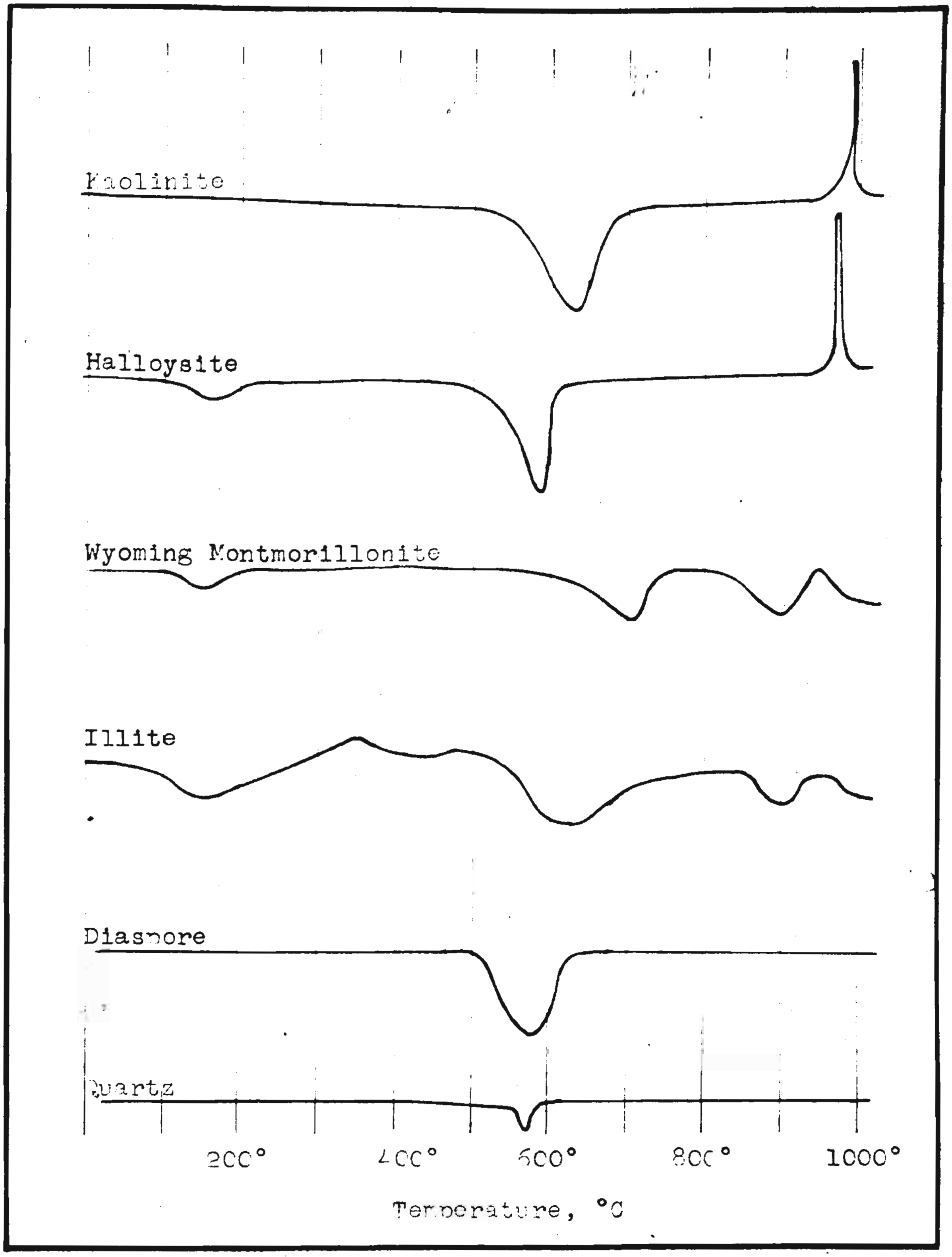

Fig. 2. Typical Differential Thermal Curves for Various Minerals

additions of curves for individual minerals. Where the peak for one constituent mineral lies at a point where no reactions occur for any other present, identification of this mineral is fairly easy.

Figure 3, page 30, shows examples of the differential thermal analysis of some typical clays.

Grimshaw, et. al., (72) developed what they call a 'double differential analysis' to identify small amounts of minerals present in clays. Where one is present in large amounts they add approximately this amount of pure mineral to the inert cup and any peaks formed will show up for the remaining mineral (s) .

Quantitative Differential Thermal Analysis

Norton(73) and Speil(74) have reported extensive work on quantitative determination of minerals present in clays. In each case they compare areas under the curves for pure and mixed samples. Of course, the same definite weight of sample is used in each case. Areas are expressed in, °C - seconds. If a clay sample has one or more peaks which correspond to any for pure clay minerals the fraction of the pure mineral in the clay is obtained by direct proportion

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(72) R. W. Grimshaw, E. Heaton, A. L. Roberts, The Constitution of Refractory Clays, Trans. Brit. Cer. Soc., Vol. 44, p. 76, 1945.

(73) Norton, Op. Cit., (footnote 70)

(74) Speil, Op. Cit.,

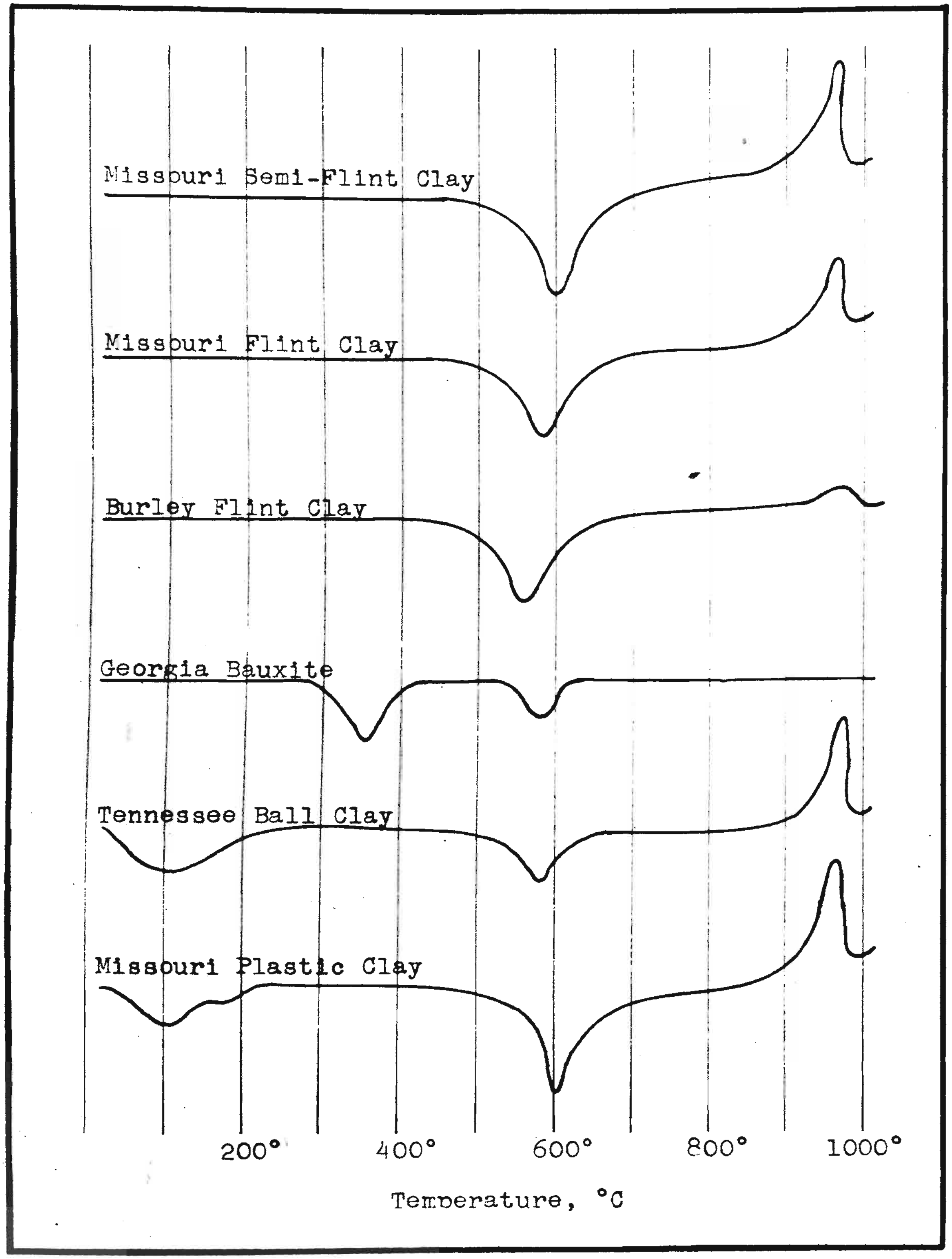

Fig. 3. Typical Differential Thermal Curves for Various Clays

of the area found to the area if the clay had been a pure mineral. Norton's results are of the order of 10% deviation from the chemical analysis.

Factors Influencing Shapes of Curves

The following factors may adversely affect the desired results of a differential thermal analysis and should be considered before drawing conclusions on any such work:(75)

(a) Decomposition of carbonates;

(b) Oxidation and conversion of vegetable (carbonaceous) matter into carbon dioxide and water.

(c) Formation of complex silicates and aluminosilicates due to bases present.

(d) Absorption of silica and alumina by those mentioned above and the formation of compounds rich in silica or alumina.

(e) Absorption and reduction of CO.

(f) Oxidation or reduction of iron compounds.

(g) Formation of solid solutions.

Particle Size and Differential Thermal Analysis

Grimshaw, et. al.,(76) noted that the size of particles makes no difference on the peak temperature though the finishing temperature of a reaction will become less with size. The high side of the curve from a peak is determined by thermal diffusivity and is not a function of the particle size.

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(75) Searle, Op. Cit., p. 392.

(76) Grimshaw, et. al., Op. Cit.

Speil(77) studied fractionated kaolin with differential thermal analysis and observed a definite adsorbed water peak for the finest sizes which was expected due to increase in surface area. The areas of the other two peaks decrease with decreasing particle size below one micron. Sharpness of endothermic peak increased as particles became smaller indicating more uniform dehydration for smaller grains. The endothermic peak also lowered for finer particles below one micron.

Norton(78) noted that the completion of the endothermic peak decreased from 670°C for 10-44 micron down to 610° for -0.1 micron while the endothermic maximum varied between 600° and 605°C.

Comparison of Differential Thermal Analysis with Other Methods

Roberts(79) reports that all studies of clays are limited by the facts that they must be made by comparison and that pure types of clays are difficult to find. Also grain size and modification of minerals in mixtures limit the comparison. Differential thermal analysis is less

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(77) Speil, Op. Cit., p. 21.

(78) Norton, Op. Cit., (footnote 70).

(79) A. L. Roberts, The Constitution of Refractory Clays, Trans. Brit. Cer. Soc., Vol. 44, pp. 69-75, 1945.

subject to these limitations than other methods.

Often chemical analysis (a long process compared to this method) does not give desired results; microscope (petrographic and electronic) and X-ray methods are limited to what they can show. Differential thermal analysis probably will long have a prominent place in the study of clay mineralogy.

Results of Differential Thermal Analysis on Flint and other Clays

Grim and Rowland(80) report a differential thermal analysis for Missouri flint clay which suggests "kaolinite is the only component; this curve, however, provides no explanation for the flint-like properties". Other closely related Missouri clays gave typical patterns as follows: burley flint, kaolinite and diaspore; plastic fire clay, kaolinite and small amount of illite; and diaspore clay, diaspore. (See the patterns for these and other clays in Figure 3, page 30.)

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(80) Grim and Rowland, Op. Cit., p. 15.

4. Petrographic Microscopy(81, 82)

One of the older methods of investigation, petrographic microscopy is useful as an aid to identifying the various crystals and other substances present in a ceramic material.

This method probably is the best yet devised for rapid qualitative determination of the larger crystals of such minerals as quartz, feldspar, mica, etc; and it is also somewhat useful in the differentiation of the three main groups of clay minerals.

The distinguishing features of the three groups are:

(a) Kaolinite group: weak birefringence and the indices of refraction approach those of quartz.

(b) Montmorillonite group: High birefringence and low indices.

(c) Hydromica group: High birefringence and higher indices.

Specific details for the principle minerals themselves are shown on page 5.

Due to the small size of the clay crystals it is often difficult to obtain specimens in random orientation which will permit study as is done with the larger minerals. To circumvent this obstruction Grim(83) has devised a method of

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(81) Searle, Op. Cit., p. 687.

(82) Rogers and Kerr, Op. Cit., pp. 352-360.

(83) R. E. Grim, The Petrographic Study of Clay Minerals--a Lab Note, Jour. Sed. Petrology, Vol. 4, pp. 45-46, 1934.

obtaining orientated aggregates of clay minerals. A suspension of the clay is made and large non-clay particles are permitted to settle out. A glass slide is suspended in the suspension and the clay collects on it. This is dried and may be shaved into thin layers for diagnosis under microscope.

Methods for making optical studies with the petrographic microscope are well covered in several textbooks, among them is that of Rogers and Kerr.

5. Electron Microscopy

One of the newer fields open to the clay mineralogist is that in which electron diffraction patterns are made in the 'electron microscope'. The sample being studied is dilutely suspended in water before being exposed to the beam of electrons which are accelerated by 50,000 volts or more. The beam of electrons is focused by two magnetic lenses. Magnifications on the order of 30,000X or more having good resolution have been made with the electron microscope.(84)

Some of the studies made on clays with this instrument may be summarized as follows;(85, 86)

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(84) R. P. Humbert and Byron Shaw, Studiesof Clay Particles with the Electron Microscope, Soil Sci., Vol. 52, pp. 481-487, 1941.

(85) B. T. Shaw and R. P. Humbert, Electron Micrographs of Clay Minerals, Soil Sci. Soc. Amer. Proc., Vol. 6, pp. 146-149, 1941.

(86) B. T. Shaw, The Nature of Colloidal Clay as Revealed by the Electron Microscope, J. Phy. Chem., Vol. 46, pp. 1032-1043, 1942.

Kaolinite is distinctly hexagonal whose individual crystals appear to be plate-like. Dispersion occurs when plates slip off larger units. Dickite has same hexagonal plates but they are thicker.

Where a sample of kaolinite was ground in water for 144 hours to minus 0.25 microns the crystals were broken and there was an absence of well-defined crystal edges.

A similar dry sample showed thicker plates but more irregular fragments due to the crystal fracture.

Halloysite was found to be composed of definite rod-like crystals which makes possible the distinction from kaolinite which is not possible using X-ray techniques. The rods of halloysite are of a definite split type.

6. <u>X-ray Diffraction Methods</u>

Sproull(87) and others have well outlined the technique and theory of X-ray diffraction as applied to mineralogical studies. Hanawalt, Rinn and Frevel(88) compiled a form that facilitated much X-ray diffraction work. They tabulated the characteristic inter-planer spacings (d-values) for each of 1000 substances. This has been amplified further by a card system(88a) for doing the same thing.

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(87) W. T. Sproull, X-rays in Practice, McGraw-Hill Book Company, N. Y., 1946.

(88) J. D. Hanawalt, H. W. Rinn, and L. K. Frevel, X-ray Diffraction Patterns, Ind. and Eng. Chem., Anal. Ed., Vol. 10, p. 457, 1938.

(88a) A.S.T.M., Standard Part I, 1942 and other editions.

Ross and Kerr(89, 90) have contributed excellent studies of the clay minerals using several methods of investigation but they were primarily concerned with the X-ray methods. They give, with other data, 34 d-values for kaolinite and over 10 for halloysite; also extensive reports on the other clay minerals, nacrite, dickite, anauxite, and allophane.

Hendricks(91) gives 13 d-values, with the probable corresponding indices, for Halloysite.

Brindley, et. al.,(92) reported the following based solely on X-ray data:

(a) Metahalloysite has the same formula as kaolinite and is of similar structure;

(b) Halloysite has two water molecules with same layers of kaolinite and metahalloysite with intervening water layer;

(c) The explanation of the low temperature dehydration is that the water layers are expelled with collapse of randomly oriented kaolinitic layers.

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(89) C. S. Ross and P. F. Kerr, The Kaolin Minerals, Professional Paper 165E, U. S. G. S., 1930. Also Jour. Amer. Cer. Soc., Vol. 13, pp. 151-160,1923.

(90) -----, Halloysite and Allophane, Prof. Paper 185G, U. S. G. S., pp. 135-148, 1934.

(91) S. B. Hendricks, Crystal Structure of Clay Minerals: Dickite, Halloysite, and Hydrated Halloysite, Amer. Mineralogist, Vol. 23, pp. 295-301, 1938.

(92) G. W. Brindley, K. Robinson, D. M. C. MacEwan, Clay Minerals: Halloysite and Metahalloysite, Nature, Vol. 157, pp. 225-226, 1946.

Correns and Mehmel(93) claim that kaolinite, halloysite, metahalloysite and montrorillonite can be differentiated by comparison of the inter-planar spacings larger than 2 Å.

Kelley(94) concludes, as have others, that "it is difficult to determine by X-ray method the several clays when present in low percentage."

7. Base Exchange Capacity Determinations(95-100)

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(93) C. W. Correns and M. Mehmel, Über den Optischen und röntgenographischen Nachweis von Kaolinite, Halloysit, und Montmorillonite, Zeitschrift für Kristallographie, Band 94, pp. 337-348, 1936.

(94) Kelley, Op. Cit., p. 117.

(95) Sante Mattson, Electrodialysis of the Colloidal Soil Material and Exchangeable Bases, Jour. Agr. Res., Vol. 33, pp. 553-557, 1926.

(96) Amar Nath Puri, Electrofiltration: A New Method of Removing Exchangeable Bases from Soil Colloids, Soil Science, Vol. 30, pp. 413-419, 1930.

(97) R. P. Graham and J. D. Sullivan, Critical Study of Methods of Determining Exchangeable Bases in Clays, Jour. Amer. Cer. Soc., Vol. 21, p. 176, 1938.

(98) G. W. Phelps, Clays-Deflocculation and Casting Control--II Clays as Minerals and as Colloids, Ceramic Age, Vol. 49, pp. 226-229, 1947.

(99) C. J. Schollenberger, and F. R. Dreibelbis, Analytical Methods in Base Exchange Investigations on Soils, Soil Science, Vol. 30, pp. 161-173, 1930.

(100) H. D. Chapman and W. P. Kelley, The Determination of the Replaceable Bases and the Base-Exchange Capacity of Soils, Soil Science, Vol. 30, pp. 391-406, 1930.

All clay and certain other minerals will adsorb, to varying degrees, cations on their surfaces or in some cases, in the crystal structure itself. The cations so adsorbed are called, 'exchangeable bases' (hence the phenomena of 'base exchange') because under certain conditions the cations adsorbed may be replaced by others.

Since the various minerals each exhibit the characteristic of being able to hold a rather definite amount of these cations the determination of the capacity of such adsorption becomes a diagnostic property of minerals and is termed the 'base exchange capacity'.

Determination of the base exchange capacity gives much information of value about a clay that aids the soil chemist and the ceramicist. Clay mineralogists have learned much about clay mineralogy by this means.

The base exchange capacity may be determined by one of several methods (dialysis, leaching, etc.) all based on the complete removal and then quantitative analysis of naturally adsorbed cations. The base exchange capacity is expressed as the number of milli-equivalents of cation adsorbed per 100 grams of clay.

Typical Base exchange capacities of various clay minerals are given on the next page.

Mineral	Me/100 gm Marshall(101)	Grim(102)
Montmorillonite	100.	60-100
Attapulgite	22.	25-30
Illite		20-40
Kaolinite	2.5	3-15
Halloysite		6-10
Nontronite	70.	

8. Combined Methods of Investigation

Bray, Grim, and Kerr(103) have presented a good summary of the various methods available; they also give a proposed new technique for studying clay mineralogy:

(a) Treat the clay to remove easily soluble materials and exchangeable bases, to permit adequate suspension of the colloid fraction. Acid is used to remove these and a three-fourths per cent solution of ammonimum hydroxide to disperse the colloids.

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(101) C. E. Marshall, Colloidal Chemistry and the Structure of Clay Minerals, Lecture given at Missouri School of Mines, Rolla, Missouri, 5 April 1949.

(102) R. E. Grim, Modern Concepts of Clay Minerals, Jour. Geol., Vol. 50, p. 250, 1942.

(103) R. H. Bray, R. E. Grim, and P. F. Kerr, Application of Clay Mineral Technique to Illinois Clay and Shale, Bul. Geol. Soc. Amer., Vol. 46, pp. 909-926, 1935.

(b) Dispersion and sedimentation to remove particles smaller than one micron followed by fraction with the super-centrifuge; fractionation into the following sizes: Residue (+1. micron), coarse colloid (ave. = 0.2 microns), fine colloid (ave. = .12 microns), and superfine colloid (-0.06 microns).

(c) Optical study of fractions with petrographic microscope.

(d) X-ray diffraction studies.

(e) Chemical analysis.

They claim that the clay minerals are not appreciably attacked by chemicals in the fraction described above. Sizes, hence, fractions changed when clays were "worked" too much and therefore did not give true natural size distribution.

Grim and Bray(104) used this method for much of the work previously reported (see page 19).

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(104) Grim and Bray, Op, Cit., pp. 307-315.

D. Relationship of Physical Properties of Clays to Mineral Composition(105)

Clay Minerals and Unfired Properties

Plasticity is favored where large numbers of small particles (with subsequent large surface areas) having large water films are present in a clay aggregate. Montmorillonite fits into this picture and as would be expected does have high plasticity. The large surface area also indicates a high water of plasticity and the attendant high drying shrinkage. The high base exchange capacity of montmorillonite indicates that the green properties will vary according to the cation adsorbed.

Illite minerals are larger than montmorillonite so the total area for possible water film is less. Plasticity, drying shrinkage, and the effect of exchangeable bases are accordingly less for illite than montmorillonite.

Attractive forces of the crystal lattices appear to be higher in illite than montmorillonite but the net effect actually is lower since units of illite are bound into larger flakes and the remaining surface charges only are taken into effect.

Replacement of aluminum for silicon in crystal lattices of illite will occur in varying degrees and this too influences properties of this mineral.

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(105) R. E. Grim, Relation of the Composition to the Properties of Clays, Jour. Amer. Cer. Soc., Vol. 22, pp. 141-151, 1939; also Circular No. 45, Illinois State Geol. Surv., 1939.

Minerals in the kaolinite group have low base exchange capacity and have little tendency to break down into the small and thin flakes that montmorillonite and illite do. In this case the low base exchange capacity may result because there is no excess charge built up on the surface due to replacement. Bond strength, drying shrinkage and plasticity are lower for kaolinite than any other clay mineral.

Grim claims that "unfired properties of clays are frequently determined to a large degree by the amount of montmorillonite or illite of a certain type which they contain". Quantities may be very small to cause a large influence on the unfired properties and this makes detection of the 'property producing' minerals difficult. Fractionation to small sizes may be necessary to study these minerals.

Clay Minerals and Fired Properties

Impurities in extremely small amount may seriously affect the firing properties of a clay but be of no importance in the unfired state. Iron which replaces alumina in the montmorillonite and illite groups will color a clay. Kaolinites are, accordingly, white-firing since iron does not replace aluminum in it.

Adsorption of ions of alkalis and alkaline earths by the high 'base exchange capacity' minerals, illite and montmorillonite, will cause a lowering of the refractoriness of the clay. These ions and iron also may be present in the lattices of illite and montmorillonite. Kaolinite, of low base exchange capacity and no replacement, will be more refractory.

III. DISCUSSION OF RESEARCH

A. Procedure:

The procedure followed in this investigation of Missouri flint clay was the same as Bray, Grim and Kerr, recommended except for certain modifications made necessary by equipment and time available and other factors which will be shown on the following pages.(106)

Missouri Flint Clay

A representative sample of Missouri flint clay on hand in the Ceramic Engineering Department of the Missouri School of Mines was used for all tests herein reported. The actual origin is in doubt but this is of little importance due to the fairly uniform nature of the typical Missouri flint clays in East Central Missouri. In fact, from the 'ceramic users' viewpoint it may quite safely be said that the clay studied is typical of all true flint clays. Each deposit will contain many arbitrary grades of clay and certain definite variations will present themselves from pit to pit, but these variations within the so-called and well-known 'flint clay' would be outside the scope of this present study.

Preparation of Samples

One small representative sample was taken of the raw Missouri flint clay and ground with mortar and pestle to minus 100 mesh and used as a standard of the tests listed later.

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(106) See page 40 for a description of this procedure.

The other samples upon which tests were made were products of the grinding operations (q. v., page 48) and were tested in the same condition as taken from ball mills and centrifuge.

Distilled water was used throughout the preparation and grinding operation. This was done to keep to a minimum ion exchange reactions which could easily render quantitative results of any kind useless. It was thought that the samples of clay so studied would exhibit characteristic properties which would be due to original substances present alone, and not to added ions or other extraneous material.

This method was also decided upon with full knowledge that complete deflocculation would be virtually impossible without added ions. Examination by petrographic microscope did not show agglomerations but particles appeared to be well deflocculated.

If, as some may think, a montmorillonite or illite mineral were present certain added ions could easily have changed the situation and might have presented a picture considerably different from the one given here. No claim is made, however, that the distilled water--no adsorbed ion method presents the true picture, either.

Grim and Bradley(107) recommend that ammonium hydroxide be used for the deflocculant where absence of a residue is sought. This was not used here, however, for the

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(107) Grim and Bradley, Op. Cit., p. 6.

reasons stated above and also that there could be no assurance that insoluble ammonium complexes would not be formed causing another source of erroneous result.

Testing of Clay

The steps taken in this study were:

(a) Wet ground three 1000 gram samples of Missouri Flint Clay in ball mills, 24, 100, and 500 hours, respectively.

(b) Determined particle size distribution in each sample.

(c) Fractionated the clays so ground.

(d) Ran the following tests on the fractions:

  (1) Petrographic analysis
  (2) X-ray diffraction analysis
  (3) Differential Thermal Analysis
  (4) Electron Microscopic examination
  (5) Chemical analysis

B. Wet Grinding of Flint Clay:

The most obvious reason for grinding a substance is to obtain a product which is more finely divided or, in other words, composed of particles having smaller sizes than the original did. In the ceramic industry this becomes, in some cases, the means to an end, which might be the complete dissemination of constituent parts of a mixture and/or increasing the plasticity or workability of a mixture.

Grinding in this case was done in order to determine, if possible, the effect of long grinding on the size of the clay particles, and also to see if the bonding material would be placed in a state that would permit isolation and identification. Plasticity developed, though known to be important in the use of flint clay, was not under study, as such. Homogeneity was assured by the long grinding.

The method employed consisted of charging each of three porcelain ball mills, one half full of balls, with 1000 grams of flint clay and adding two liters of distilled water. Then the mills were revolved for 24, 100 and 500 hours, respectively. Raw flint clay slakes poorly and incompletely in distilled water and could not be used as a standard upon which to base other findings.

C. Particle Size Distribution

Each ground sample was seived through 325-mesh and it was observed that there was very little residue of any kind. What little residue remained amounted to less than 1 gram (or less than 0.1%) and appeared largely as a jelly-like mass when wet and as a net of hair-like fibers when dry. This sample is called, +325-mesh or (+44 microns) on the tests reported later.

Particle size distribution was determined on the other samples by Andreasen pipette method.(108) At first it was thought the Dotts tube of the Kelly type would be the best method available but preliminary studies bore out the contention of Loomis that this method is generally unsatisfactory.(109)

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(108) See pages 16-17.

(109) See pages 12-13.

Samples were checked, to develop technique and to perfect the method, until three concurrent runs agreed to within about 2% (i. e., per cent finer), this being considered sufficiently accurate for this purpose. It is doubted that greater accuracy could be expected with this method notwithstanding the claim of Krumbein of 1% checks.(110) One improvement was noted when eleven sizes were taken in the test rather than the usually recommended six. This seemed to improve sensitivity and accuracy.

The average of the three runs was taken for each of the three samples and this is reported on Tables I-III. Preliminary runs are not reported.

Standard surface factor was determined for the three samples based on the average per cent finer values and is reported as Table IV.

A summary for convenient comparison is made on Table V, Page 54, and a plot on Fig. 4, Page 55 gives a graphical representation.

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(110) See page 17.

Table I

Particle Size Distribution for Missouri Flint Clay

Ground 24 Hours

Particle Size (Microns)	Per Cent Finer 1	2	3	Ave.
20	98.45	100.64	100.14	99.74
14	111.54 (?)	101.78	100.68	100.+
10	95.90	104.32 (?)	98.80	99.67
7	94.36	95.93	95.03	95.11
5	86.66	88.04	84.01	86.24
3.2	75.51	75.83	76.35	75.89
2.0	63.72	63.23	62.37	63.11
1.4	55.26	55.85	55.92	55.68
1.0	47.82	46.18	47.05	47.02
.7	40.90	40.08	39.92	40.30
.5	29.10	29.01	29.30	29.14

Table II

Particle Size Distribution for Missouri Flint Clay

Ground 100 Hours

Particle Size (Microns)	Per Cent Finer 1	2	3	Ave.
20	99.11	98.45	98.56	98.71
14	99.87	99.06	97.65	98.86
10	98.10	98.09	98.04	98.07
7	97.59	96.76	95.83	96.73
5	89.75	91.66	92.70	91.27
3.2	78.86	80.73	80.72	80.10
1.4	50.25	52.57	51.30	51.37
1.0	36.83	40.79	39.58	39.07
.7	28.10	29.37	28.12	28.75
.5	19.49	18.70	19.14	19.11

Table III

Particle Size Distribution for Missouri Flint Clay

Ground 500 Hours

Particle Size (Microns)	Per Cent Finer			
	1	2	3	Ave.
20	99.11	98.90	99.58	99.19
14	98.98	99.75	100.38	99.70
10	100.25	102.81	99.19	100.+
7	87.42	99.14	98.66	98.90
5	86.40	98.29	97.87	98.08
3.2	94.28	93.89	94.97	94.28
2.0	79.92	81.66	81.79	81.12
1.4	67.98	69.56	69.64	69.06
1.0	53.37	56.85	53.42	54.55
.7	39.39	41.08	38.65	39.71
.5	24.40	24.33	24.67	24.46

Table IV

Surface Factors for Intervals between Grain Sizes Reported on Tables I-III

		24-Hour		100-Hour		500-Hour	
S	D	W	W/D	W	W/D	W	W/D
20-14	17.15	(All particles assumed smaller than 10 microns)					
14-10	12.1						
10-7	8.6	.0489	.0057	.0337	.0039	.0110	.0013
7-5	6.05	.0887	.0147	.0546	.0095	.0082	.0014
5-3.2	4.16	.1035	.0248	.1117	.0268	.0380	.0091
3.2-1.4	2.42	.2021	.0835	.2873	.1185	.2522	.1041
1.4-1	1.21	.0866	.0716	.1230	.1018	.1451	.1200
1.-.7	.86	.0672	.0781	.1032	.1210	.1484	.1726
.7-.5	.605	.1116	.1845	.0954	.1561	.1525	.2520
.5-.03	.149	.2914	1.9550	.1911	1.280	.2446	1.6410
Summation		1.00	2.4229	1.00	1.8156	1.00	2.3015
Standard Surface Factor	$X10^{-4}$		5.60		4.19		5.31

(expressed in square centimeters/gram)

Explanation of Symbols:

S = Size Interval in microns

D = Average diameter of the size interval

W = Weight in size interval

Table V

Summary of Particle Size Distribution Data Taken From Tables I-IV. See Fig. 4, Page 55 For Particle Size Distribution Curves for These Data

Particle Size (Microns)	Per Cent Finer Values 24 Hour	100 Hour	500 Hour
20	99.74	98.71	99.19
14	100.+	98.86	99.70
10	99.67	98.07	100.+
7	95.11	96.73	98.90
5	86.24	91.27	98.08
3.2	75.89	80.10	94.28
2.0	63.11	---	81.12
1.4	55.68	51.37	69.06
1.0	47.02	39.07	54.55
.7	40.30	28.75	39.71
.5	29.14	19.11	24.46
Standard Surface Factor $(\mathrm{CM}^2/\mathrm{gm}) \times 10^{-4}$	5.60	4.19	5.31

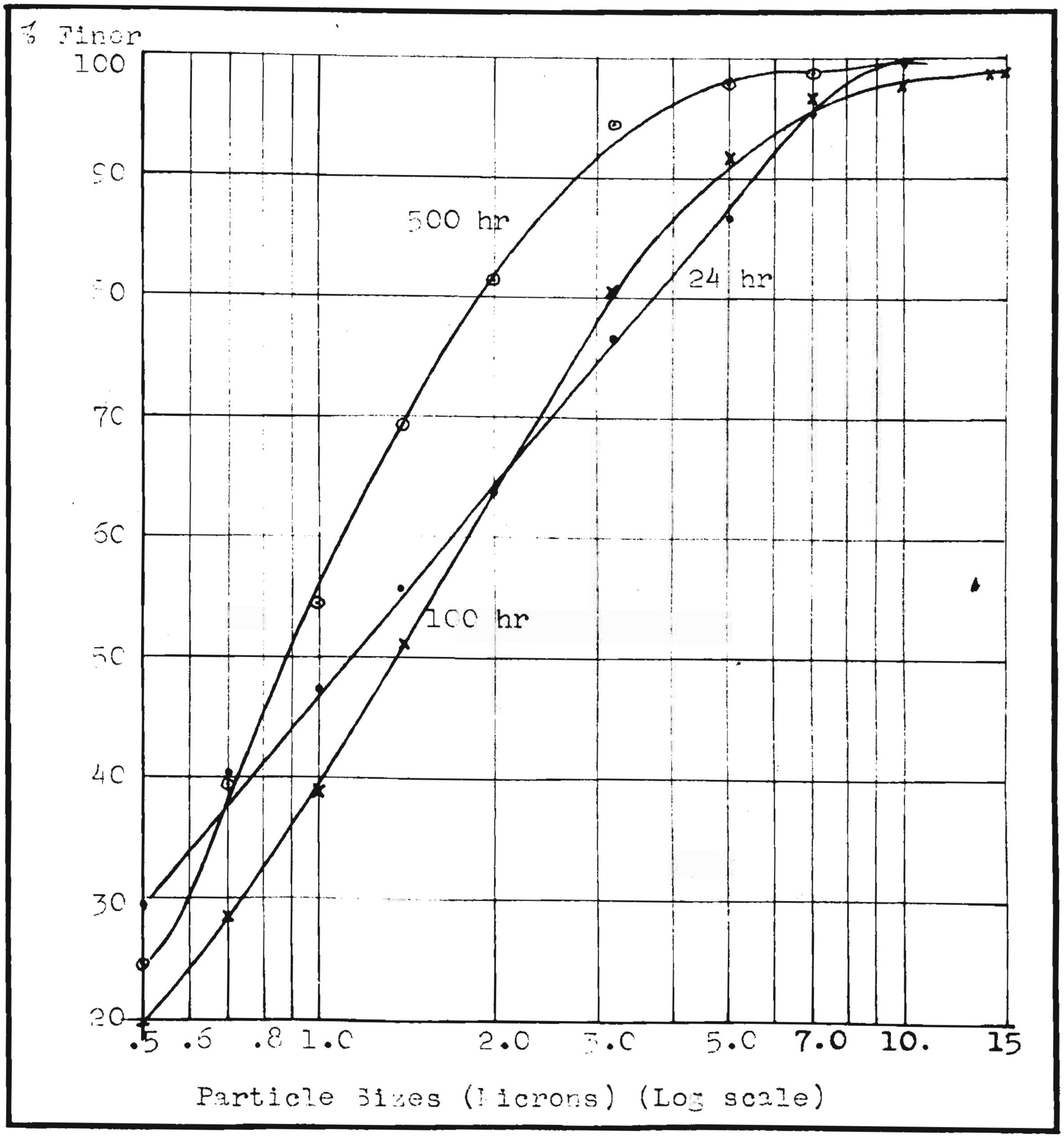

Fig. 4. Graph showing results of particle size distribution determinations on ground samples of Missouri flint clay.

Equivalent Spherical Diameter

In all cases where non-spherical particle sizes are measured utilizing Stokes' law the term "equivalent spherical diameter" should be used to indicate the sizes so measured. This is because any non-spherically shaped particle falling in a liquid medium will fall more slowly than spheres of the same mass and volume. True size and mass will, accordingly, be larger than that calculated according to Stokes' law. It must be remembered, then, that the 'equivalent spherical diameter' refers to the size of a spherical particle which would settle in a certain time and that the corresponding non-spherical particle which settles in this time will have a larger volume and greater mass than calculated. The explanation of this for clay particles is that at least one dimension is considerably larger than one of the others and as Kunkel(111) explains, this calculation for these very thin plates will be over 50% in error. The system using equivalent spherical diameter, though not yielding true values, is useful for comparative purposes and is a common practice in reporting on clay mineralogy.

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(111) W. B. Kunkel, Magnitude and Character of Errors Produced by Shape Factors in Stokes' Law Estimates of Particle Radius, Jour. Applied Physics, Vol. 19, pp. 1056-1058, 1948.

Results of Grinding and Particle Size Determination

The slope on the particle size distribution curve is indicative of the weight of particles which are present in a given range; e.g., at the place where a slope approaches zero almost no particles are present and where the slope is steeper more particles are present. Figure 5 shows two typical particle size distribution curves where one represents a greater weight of particles finer for all sizes throughout entire range than does the other.

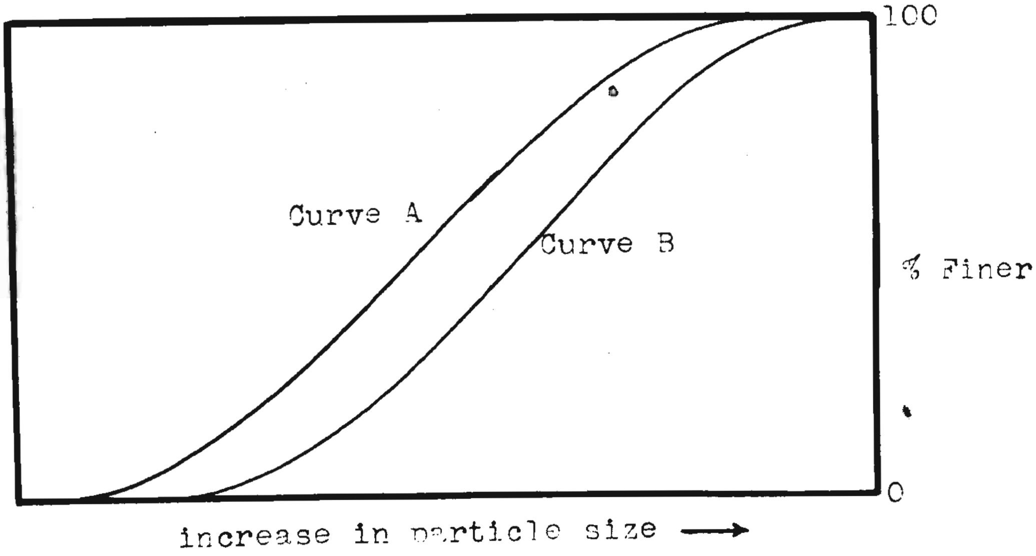

Fig. 5. Particle Size Distribution Curves:

Curve A has a greater weight of particles finer for all sizes throughout than does Curve B.

Figure 6 shows the case where, due to different particle size distribution, two curves may intersect.

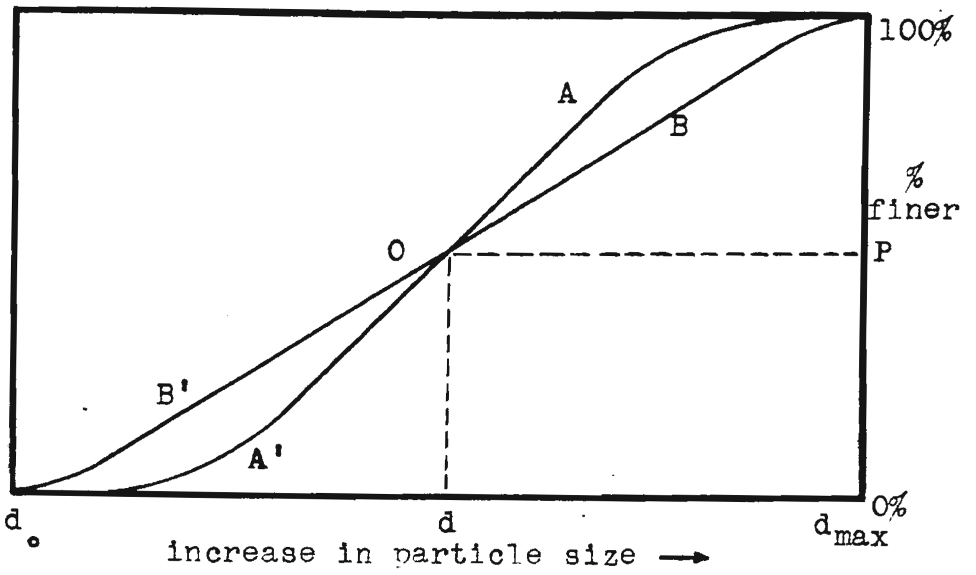

Fig. 6. Particle Size Distribution Curves.

That portion of the curves (shown on Figure 6) above P can be treated as with Fig. 5; that portion below P indicates that B has a greater weight of particles finer than A for the range d_o - d. The intersection of curves A and B, at O, is one in which both A and B contain the same weight of particles whose size is less than d. The difference between the two curves is that A has a greater concentration (due to greater slope) of particles in the vicinity of d than does B; and B has more particles (due to greater slope) in both ends of the curve than does A.

Figure 4, the plotted results of this study, is shown in Fig. 7 with supposed extensions to a 'zero per cent finer' for smallest particle size present. These extensions

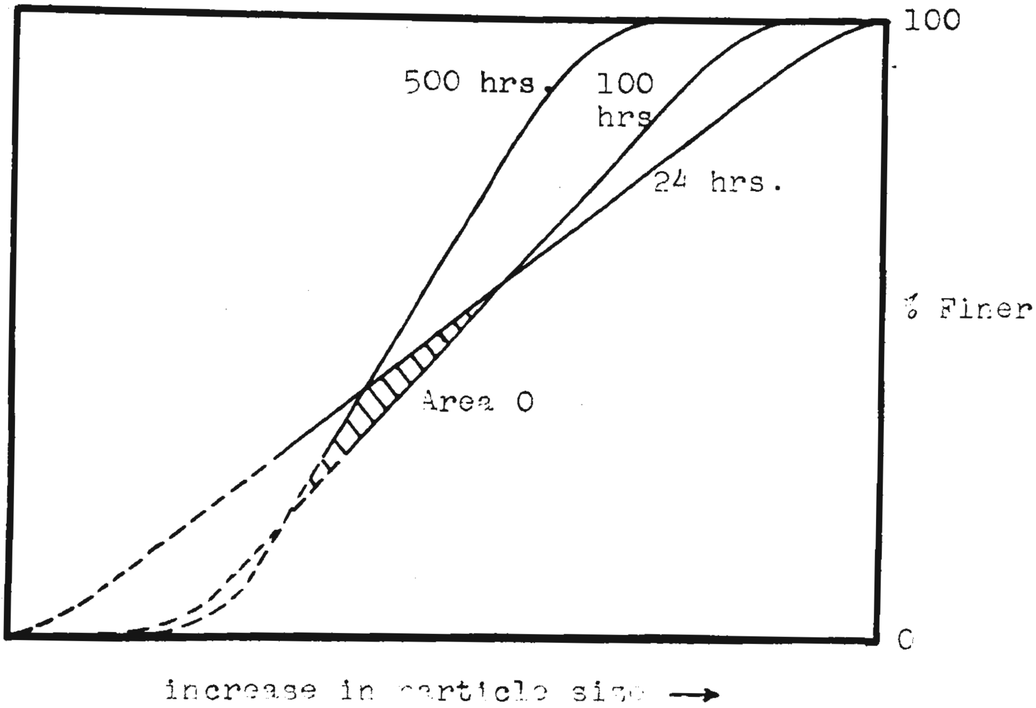

Fig. 7. Particle Size Distribution Curve of Missouri Flint Clay showing effect of long grinding. (Not to scale)

show an additional intersection which forms the area O, which is not unlike the point of intersection O in Fig. 6. For an ideal case it may be assumed that curves of Fig. 7 would intersect in a point. The explanation of curves in Fig. 7 can be made by direct application of the rules shown for Fig. 6.

The significance of these curves is, however, more complex since all three curves are for essentially the same material, the differences being length of time each sample was ground. Taken all together it may be said that that portion of Fig. 7 above and to the right of the area O follows the normal character of grinding time curves where an increased time produces an increased quantity of fine particles (see Fig. 5).

Below and to the left of the area O one sees that the curve indicating least grinding has a greater weight finer and vice versa. And since, for each individual intersection and a hypothetical common intersection of all three curves, each sample shows the same weight of particles which are finer than the corresponding size, it follows that there has been a reduction in the weight of finest particles (observed in 24-hour curve) in the case of that which was ground the longest. This must mean, then, that an agglomeration or flocculation has occurred (to account for loss in finest particles) as grinding proceeded. The range in which these new particles have formed is approximately 0.7 to 3.0 microns as indicated by slopes on Fig. 4.

The fact that the intermediate grinding time of 100 hours is present fully substantiates the discussion presented. All three grinding times are purely arbitrary and do not necessarily indicate any boundaries. It might be assumed that the limiting case for length of grinding would be when all particles had been broken so as to fall within the range of agglomerate sizes and the resulting curve would be extremely flat on each end and very steep in the agglomerate range. The other limiting case is, of course, for a vertical line at the gross size limit where no comminution had occurred. The reason for the apparent agglomeration is not so easy to explain and is studied in subsequent sections.

D. Fractionation of Missouri Flint Clay

It has been indicated that various investigators(112) use fractionation in the study of clays because it has been shown that certain clay minerals occur largely in definite size ranges and also because small amounts of certain minerals which may lie in a very narrow size range often have a great effect upon the bulk clay sample.

Fractionation in this case was accomplished as follows:

(a) All except a very small residue (page 48) passed 325-mesh sieve (44 microns).

(b) The fraction -44, +1 microns was obtained by settling. (As indicated on Fig. 4 and Table 5, approximately 50% of the sample fell in this range.)

(c) Sharples Super Centrifuge was used to make all other fractions, viz., 1.0-0.3, 0.3-0.2, 0.2-0.1, and 0.1-0.05 microns.

Entire -1 micron sample was run through centrifuge which was operated to give cutoff for smaller size and this effluent was run through for next cutoff, etc.

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(112) See pages 18-19.

These fractions compare favorably with those recommended by Grim and Bray(112).

Examination of the fractions was made by petrographic microscope, X-ray diffraction, differential thermal analysis, electron microscope, and chemical analysis and is discussed hereafter.

E. Petrographic Microscope

Use of the petrographic microscope was limited in this study to examination of deflocculation (page 46) and to the examination of the +325-mesh (+44 microns) residue.

The latter revealed the following minerals as being present: quartz; an opaque mineral which probably was magnetite; a hair-mat form not identified positively as mineral matter; and a clay mineral aggregate.

The first two named may not have been present in the raw clay, but were likely impurities picked up in transit. Their very small amount compared to the amount of clay from which they were separated would indicate little importance.

The most interesting feature is the hair-mat form present. Before drying a gel-like substance appeared on the sieve and this quite likely was the parent from which the hair-mat came. If this was, by chance, mineral matter it could possibly have come from silica or alumina gels. What is more likely, however, is that this, too, was impurity possibly in the form of woody, paper or cloth matter which was also picked up in the transportation. This contention is borne out in chemical and other tests.

The clay aggregate probably was actually composed of particles smaller than 44 microns but due to the hair-mat this was retained on the 325-mesh and dried as an aggregate which appeared opaque due to large sizes under petrographic microscope.

It must be remembered, again, that the total residue on 325-mesh was very small and it is doubted that any so retained and observed could contribute to the mineralogical and ceramic nature of Missouri flint clay.

F. X-ray Examination

All samples made and studied in the previous sections were analyzed in the X-ray diffraction spectrometer and the resulting d-values were all compared. Only two different sets of results, however, were obtained; all fractions agreed so closely with the original raw flint clay as to render differentiation virtually impossible. Occasional and slight differences could be detected but it is thought that these were no more than instrument variations. The residue collected on the 325-mesh sieve, previously described, did exhibit a few distinct d-values and these are reported for comparison and as a clue to the content of the residue.

Table VI, on the next page, shows a comparison of d-values for the Missouri flint clay and the more prob-

TABLE VI. Principle Inter-planer Spacings (d-values) for Various Clay and Associated Minerals, including Missouri Flint Clay

Kaolinite		Halloysite		Meta-Halloysite	Diaspore	Quartz	Gibbsite	Mont-Morillonite	Mo. Flint	Residue
(113)	(114)	(114)	(113)	(114)	(115)	(115)	(115)	(114)	(116)	(117)
								13.0		
	7.16		7.42	7.46						
									7.01	
							4.78			
4.46	4.39	4.46	4.42	4.41						
								4.37	4.345	
4.194	4.17									
						4.25	4.24		4.1	4.29
3.874			3.97		3.99					
3.614	3.56		3.63	3.63						
									3.51	
3.424	3.36	3.40								
						3.35	3.31		3.305	3.34
							3.12	3.13		3.2
							3.07			
							2.81	2.92		
2.512	2.55	2.56	2.56	2.55						
						2.45	2.55	2.58	2.53	
2.344			2.365							
							2.43		2.49	2.46
2.305					2.31					
						2.23	2.27		2.315	
2.005					2.12					
							2.15		2.185	2.155
					2.06					
									1.985	1.962
						1.82			1.885	
					1.71					
									1.80	1.775
1.666			1.685		1.63					
									1.651	1.645
1.487			1.510		1.477					
						1.54			1.485	
					1.420					
									1.45	
1.347					1.370					
						1.375				1.37
			1.295							
									1.29	1.334
1.283										
									1.282	
1.233			1.250							
									1.238	

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(113) C. S. Ross and P. F. Kerr, Op. Cit.

(114) C. W. Correns and M. Mehmel, Op. Cit., pp. 33 -348.

(115) Hanawalt, et al., Op. Cit.

(116) Samples run by the author in the M.S.M. Ceram c Engr. Dept.

(117) This sample was the +325 mesh residue describ d elsewhere.

able constituent and associated minerals. The tabulation shows lack of agreement among the 'authorities' on the actual d-values for kaolinite and halloysite and would indicate a certain un-reliability for the others reported.

The Missouri flint clay appears to fit the kaolinite values best though there is no positive proof that one or more of the other minerals is not present. Montmorillonite has been suggested as a small but important constituent but certain principle montomorillonite lines are not observed in the flint clay.

The closeness of the halloysite and kaolinite lines precludes a sharp differentiation in this case though some prominent halloysite lines (7.42, 3.97, 3.63, 2.365, 1.510, 1.250) are not observed. Other lines would be masked by the kaolinite lines or vice versa.

It appears that the petrographic discovery of quartz in the residue is born out in this instance. No clue to the origin of this quartz is to be found here, however.

G. Differential Thermal Analysis

As in the case of X-ray examination all samples were examined by differential thermal analysis. The apparatus used for this purpose is the one described by Herold and Planje(118) with a few changes. The sample holder used was made entirely of alumina.

Each sample was run twice but not consecutively to

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(118) Herold and Planje, Op. Cit., pp. 20-22.

serve as a check of the recorded patterns. Very good checks were obtained for all samples.

The raw flint clay, dry ground just enough to pass 100-mesh sieve, gave the typical kaolinite pattern with a distinct endothermic peak in the 560-580°C region and a sharp exothermic peak at 960-980°C. A small endothermic peak was observed at 80°C and probably was the removal of the small amount of mechanically held water. No peculiarities were to be noted on these patterns. All other samples gave patterns the same as the above except as noted below.

Both runs of the whole 24-hour ground sample showed a short leveling of the curve on the high side of the 560-580° peak which may have indicated a small amount of montmorillonite or other mineral to be present. This is shown on figure 8 and looks exactly as the curve reported by Grimshaw, et. al.,(119) in which montmorillonite was claimed to be present with kaolinite.

No reproduction of this condition was present in any other sample tested and the presence or absence of montmorillonite was not further indicated by differential thermal analysis.

Samples of the 100- and 500-hour clays gave patterns practically identical to the raw, un-ground, flint clay.

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(119) Grimshaw, Heaton, and Roberts, Op.Cit., p. 76.

The only visible change that the samples of the fractions gave was the expected progressive decrease in the intensities of the peaks with a decrease in particle size. No new peaks were anywhere present.

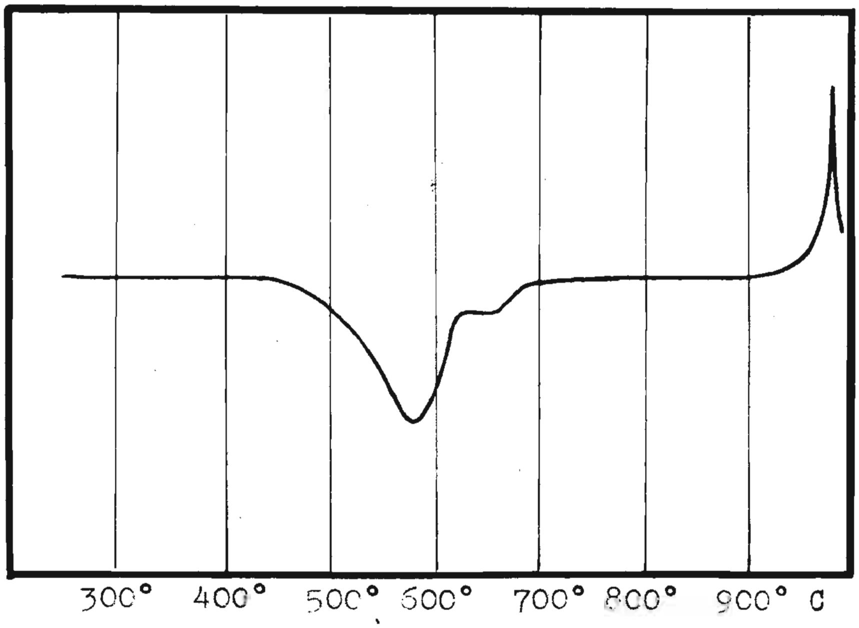

Fig. 8. **Differential Thermal Analysis Pattern For 24-hour wet ground Missouri Flint Clay.**

No particular significance is attached to the temperatures of the peaks found in this study for they are well within the range of those reported in the literature. Whether the kaolinite peak occurs at 550°, 620° or between these limits depends more on the apparatus and technique used than on any other factors.

H. Electron Microscopic Examination

Three of the smaller fractions, viz., .05 to 0.1, 0.2 to 0.3, and 0.3 to 1.0 microns, were prepared and examined with the University of Missouri electron microscope(120). The purpose of this examination was two-fold: first of all, the shape of the particles was thought to give a clue to the mineralogical identification, and, secondly, the effect of grinding on particles was to be studied. Five microphotographs (X6250) were taken of each of the three samples and two representative photos of each (X12500) are shown on Figure 9, page 69.

A careful comparison of these photos with those reported in the literature(121, 122, 123) shows conclusively that kaolinite is the most prominent, if not the principle, mineral in Missouri flint clay. The hexagonally shaped plates clearly identify the kaolinite.

An examination of Fig. 9 shows the typical kaolinite plates in all three sizes. There appears to be a lessening of the definite shape, however, for the finest size;

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(120) Under the direction of Dr. N. S. Gingrich, Department of Physics, University of Missouri, Columbia, Mo.

(121) Laws and Page, Op. Cit.

(122) Shaw, Op. Cit.

(123) Shaw and Humbert, Op. Cit.

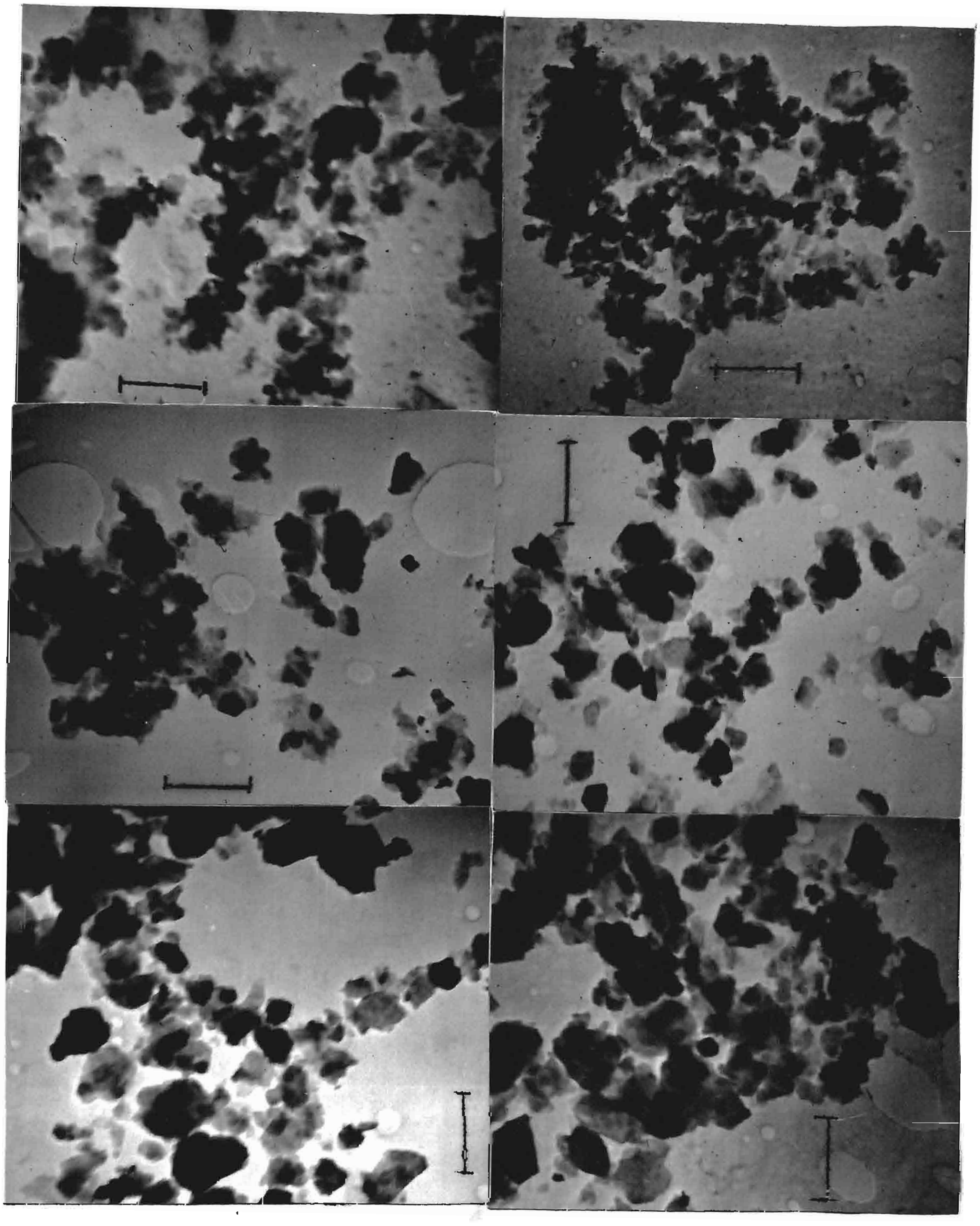

Fig. 9. (X12,500) Electron Microphotographs of Fractions of Ground Missouri Flint Clay. Top: .05 to .1 microns; middle: .2 to .3 microns; bottom: .3 to 1.0 microns. (Line indicates one micron). (Microscopy by Dept. of Physics, U. of Missouri, Columbia, Missouri.)

this would be expected when the plates themselves are fractured.

The thin character of the plates is evident where partial slippage of plates has occurred. Accordingly the largest sizes may be said to be composed of thin individual plates, multi-layered crystals and agglomerates of crystals. The middle and small sizes show fewer agglomerates.

That the fractionation was fairly accurate is indicated by comparison of the equivalent spherical particle sizes and the micron scales furnished by the microscopist. That fractionation was not quite complete is attested to by the small particles with the larger samples.

The sizes of the hexagonal plates shows that kaolinite exists in plates of about .05 to at least 0.8 microns. Agglomerates containing all sizes were composed of mixtures of the small and the large plates as well as fractured crystals.

I. Chemical Analysis

In an effort to ascertain any chemical differences and the possible mineralogical reasons therefor, chemical analyses were run for all fractions and samples made.(124) The tabulated results appear on page 72 and a comparative graph is on Fig. 10, page 71.

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(124) Analyst, Mr. Donald L. Heath, Missouri Clay Testing Laboratory of which Dr. Paul G. Herold is director.

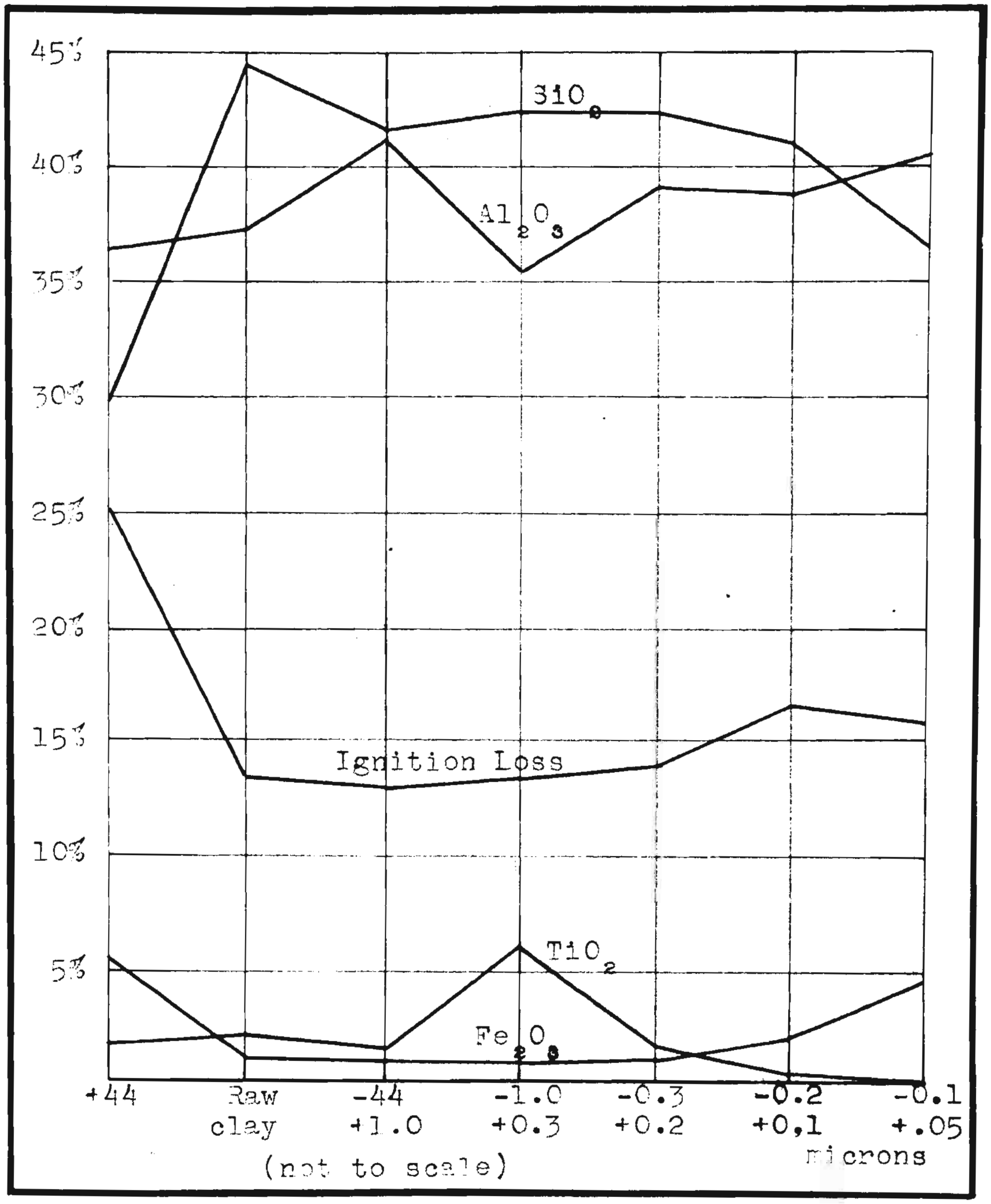

Fig. 10. Plot of the Percentage Compositions for Various Fractions of Missouri Flint Clay.

Table VII. Chemical Analysis of Missouri Flint Clay

	+44 residue	Raw Flint	-44 +1.0	-1.0 +0.3	-0.3 +0.2	-0.2 +0.1	-0.1 +.05 microns
SiO_2	29.80	44.41	41.6	42.55	42.44	41.02	36.30
Al_2O_3	36.3	37.1	41.1	35.4	39.1	38.7	41.5
Fe_2O_3	5.63	1.10	.98	.88	1.07	1.85	4.61
TiO_2	1.75	2.31	1.40	6.02	1.75	tr.	0.00
Loss on Ignition	25.23	13.41	13.19	13.43	13.88	16.68	15.71
Total	98.61	98.33	98.27	98.28	98.24	98.25	98.12

The chief reason for less than 100% values is the fact that alkali and alkaline earth oxides were not analyzed.

The extremely high loss on ignition for the +44 micron (+325 mesh residue) bears out the previous contention that organic matter probably was present in this sample. The previously noted result that quartz and kaolinite were present seems to indicate that part of the alumina present was actually an alumina gel, not identified by other methods. The high iron content was probably the opaque hematite noted by petrographic microscope.

The vast differences in weights obtained for the various samples tends to cloud the chemical picture considerably and prevents a scalar evaluation. For example, the raw flint represents, of course, 100% of the clay while the -0.1 and +44 micron sizes represent less than 1% each.

The -44+1.0 size represents some 50% while approximately 20-30% was present -1.0+0.3 microns. Nevertheless, Fig. 10 does show some noteworthy relationships in chemical composition with decrease in particle size.

Perhaps the most outstanding feature is the very high concentration (6.02%) of titania in the one, -1.0+.3 micron, fraction. It is also interesting that little to no titania is present -.2 microns. It is not known which mineral is responsible for this titania.

The high iron content for the smallest sizes may be indicative of mineralogical changes but it is more likely a sign of impurities picked up in collecting these samples. The fractionation proceeded in the super-centrifuge in such a manner that the sample collected on the liner was scraped off, blunged and re-run for a smaller cutoff until the finest size was reached. In other words the smallest size was re-run several times in the centrifuge before final separation. It was noted that a definite darkening of the sample took place at the bottom of the liner each time and this was attributed to metallic stain resulting from the wear of the metallic surfaces at the bottom of the centrifuge bowl. In the larger sized samples the darkened clay was discarded but in the last one this was retained due to the very small amount of clay present.

If this higher iron content were due to naturally occurring iron it might be analogous to the higher alumina content also noted for the -0.1 micron size. Since these did not show up as distinct minerals it may be assumed that both alumina and iron hydroxides were present in small amount.

The progressive drop in the silica content for decrease in particle size and the steep drop at the lower end is another outstanding feature. One rather obvious question is, what became of the silica, if each fraction contained a lower percentage than did the original clay? No answer is as readily forthcoming. Silica is not soluble in acids (other than HF) and only very slightly soluble in alkalis so silica, as such, apparently was not dissolved and lost in discarded water. Desilication of silicates is not an unknown phenomenon but the problem in this case is more than simple desilication of the kaolinite; silica is actually removed. One possible answer would be combination of silica, or one of its acids, with alkali present to make a soluble compound.

Another possibility is that of the silica remaining in suspension -.05 microns, in which case one would expect to find a very high percentage of SiO_2 since very little -.05 was to be observed in the effluent after the -.05 cutoff. This is contraindicated as the silica content falls off rapidly from -.3 to -.05; if silica were to be expected in the -.05 one would expect an increase from -.3 to -.05, also.

The condition of alumina is somewhat opposed to that of silica; all of the alumina values except -1+.3 are higher than the alumina of the raw flint. This would not look so formidable were it not for the very much higher alumina in the sample present in largest amount (viz., -44+1.0). It is not unreasonable to assume that analytical errors may have given such a high value for the one alumina sample.

Recalculation, assuming that all of the clay, except ferric oxide, titania, and all unreported oxides, would be pure kaolinite, gave the following: the raw flint and -1+.3 were almost perfectly balanced according to the theoretical alumina:silica:water ratios of 39.6:46.5:13.96. All other silica values for the fractions were lower than theoretical 46.5%. The -.2+.1 alumina was same as theoretical and -.3+.2 was close. Alumina was generally higher than the theoretical 39.6%. The actual loss on ignition was the same as the theoretical 13.96% for all fractions except the smallest two sizes where actual exceeded theoretical kaolinite values.

The latter bears out the previous statement that alumina and iron hydroxides were probably present in -.1+.05 fraction. The decrease in quartz from theoretical kaolinite values is more important when one considers the increase of loss on ignition and alumina combined. If all silica of -.1+.05 were in kaolinite only 30.9% of alumina and 10.9% of the water would be tied up in kaolinite. The remaining 10.6% alumina and 4.81% water could yield 12.4% $Al_2O_3 \cdot H_2O$ and leave 2.94% H_2O remaining.

IV. CONCLUSIONS

The wet grinding of Missouri flint clay produces, for short periods of grinding, an increasing amount of smaller particles. For a certain range longer grinding shows that an agglomeration of the finer sizes actually occurs. Twenty-four hours appears to be within the short period while 100 hours appears to be in the longer range. The agglomeration is in the range of about 0.7 to 3.0 microns.

The chief mineral present in Missouri flint clay is kaolinite. This is confirmed quite conclusively by X-ray, differential thermal, electron microscopic and chemical methods. No other minerals were positively identified as being present in the clay, though there is a definite indication of aluminum hydroxide in the finest fractions.

The evidence, chiefly chemical, points to the conclusion that alumina gel is probably the agent which is responsible for the hardness of Missouri flint clay. It is assumed that the bonding material would be present chiefly in the smallest fractions and it was noted that alumina was increased (while silica decreased) in the two smallest sized fractions present.

Titania, which is present in small amount in Missouri flint clay, was found concentrated in the 0.3 to 1.0 micron fraction after grinding. Mineralogy was not determined for the titania.

Grinding of kaolinite crystals causes, first of all, the slippage of the small kaolinite plates along the cleavage plane. Finer grinding brings about actual fracture of the plates perpendicular to the cleavage plane.

X-ray and differential thermal techniques did not offer sufficient information to make mineralogical differentiation of the fractions of clay.

V. SUMMARY

Separate samples of Missouri flint clay were wet-ground in a ball mill for 24-, 100-, and 500-hours, respectively. The particle size distribution for each of these samples was determined using the Andreasen pipette method. It was found that there was a greater weight of 0.7-3.0 micron size particles in the 500-hour than in the 100-hour and in the 100-hour than in the 24-hour grinds; while the reverse was true for the particles larger than 3.0 microns and smaller than .7 microns; this indicating agglomeration with long grinding.

Fractions of the ground clay were made and each studied extensively by X-ray diffraction, differential thermal, petrographic, electron microscopic and chemical analyses. These methods were employed to help identify the clay and other minerals present in the fractions. X-ray diffraction and differential thermal analysis gave typical kaolinite patterns while the electron microscope gave actual photos of the kaolinite crystals. The petrographic microscope helped to identify quartz in the residue (+44microns) but failed to help in other fractions.

Actual differentiation of constituents in the fractions was possible only by chemical analysis where it was learned that an increase of alumina with decrease of ~~quartz~~ silica EPH is found in the finer fractions. Titania was isolated largely in the 0.3 to 1.0 micron fraction.

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Vita

EDMOND PRESTON HYATT, oldest of three children of Clarence E. and Belle A. Edmonds Hyatt, was born 15 November 1923 in Joliet, Illinois. He attended Joliet public schools (except for two years in the Hastings, Michigan, public schools) graduating from Joliet Township High School 4 June 1942.

He entered Missouri School of Mines in September 1942 and signed with the Enlisted Reserve Corps, Army of the United States, 24 October 1942; was called to active duty in March 1943 and served in the Corps of Engineers until 7 July 1946. On 9 February 1944 he graduated from Fort Belvoir, Virginia, Officer Candidate School. He served in training positions in the United States until March 1945 when he was sent to serve in the India-Burma Theater of Operations. He was a First Lieutenant when placed on inactive duty by the army.

Army Nurse Ora Mae Sorensen, of Manti, Utah, became his wife on 26 February 1945. Three children have been born to them: Nancy Mae, 21 February 1947; Carol Ann, 11 July 1948; and Theodore Preston, 3 January 1950.

He re-entered MSM in September 1946 and received his degree of Bachelor of Science in Ceramic Engineering in May 1949, though all requirements for this were completed in January 1949. As an undergraduate he became a member of Tau Beta Pi, Phi Kappa Phi, Keramos, and the American

Ceramic Society. He was awarded a certificate as the Honor Graduate in Ceramic Engineering for the year 1949 and graduated with First Honors in his class.

He undertook graduate studies in January 1949 as a Graduate Research Fellow and continued through Spring, Summer, and Fall 1949.

During most of his residence at Missouri School of Mines he served as President of the Rolla Branch, Church of Jesus Christ of Latter-day Saints.