Diffusion of Light by Colloidal Clay Suspensions

A Thesis presented to the Faculty of the Virginia Agricultural and Mechanical College and Polytechnic Institute as a partial fulfillment of the requirements for the degree of Master of Science in Chemistry

by

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This thesis is dedicated

to Dr. Philip C. Scherer, Jr.

whose kind help and encouragement

throughout the work has been un-

ceasing.

Diffusion of Light by Colloidal Clay Suspensions

The purpose of this work is to find a method of determining the average particle size in samples of clays and ceramical materials, and to attempt to classify their physical properties according to the size of the particles. Such data should be useful to compare the properties of clays, to match different samples for uniformity, and to better control processes where clays are used, as for instance in manufacture of paper, rubber, and burned wear.

High frequency light radiation or xrays and visible light have been applied to different methods for comparing and measuring particle size. A great deal more work has been done using the x-rays than the visible light. In fact, this latter method has been quite neglected in recent research.

Rudolf Brill determined (1) the size of small particles from the broadening of the x-ray spectral lines. He compares the methods of Scherrer and of von Laue and finds the former method useful only for relative small particles with strong absorption.

Aborn and Davidson (2) examined classified silica particles by powder diffraction method using the unfiltered radiation of a Coolidge Molybdinum target. He observed qualitative differences in differential patterns with varying size distribution and the same average particle size. Microphotometric analysis of the patterns indicate that a quanitative relationship between characteristics and average particle size can be obtained if the size distribution is kept constant.

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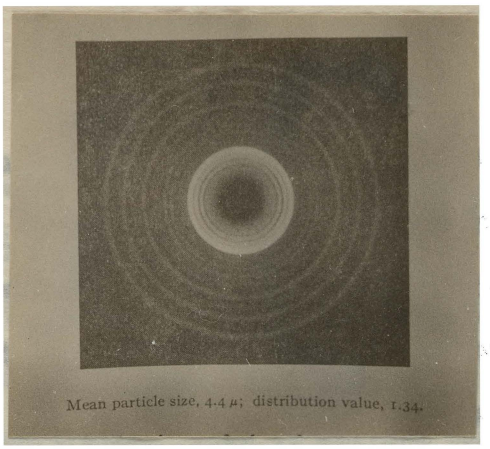
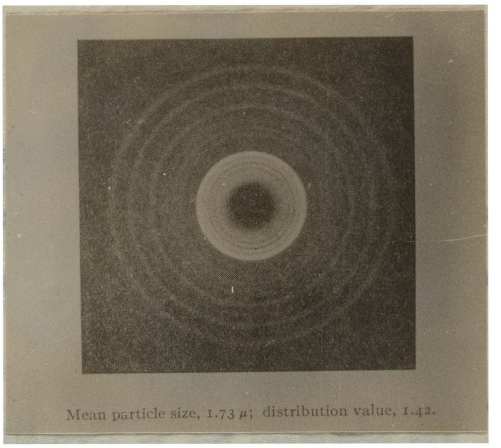
(1) Rudolf Brill; Z. Krist. 68 387-403 (1928)

(2) Aborn and Davidson; J. Franklin Inst. 208 #1 1929 p59



Mean particle size, 4.4 μ; distribution value, 1.34.



Mean particle size, 1.73 μ; distribution value, 1.42.

Plate 1

Plate 1 shows two photographs of the patterns obtained by Aborn and Davidson from two different samples of the indicated size and distribution. A densitiometer was used to determine in the outer band the density change,and it was found that for each variation in size and distribution characteristic variations in the microphotometric graph was obtained. This difference however, could not be corrilated with quantitative measurements.

M. von Loue reports an x-ray method for determining the size (3) and shape of crystalline ultramicroscopic particles.

H. Mark (4) discusses equations for particle determination agreeing with experiment for the case of parallel radiation and non-absorbing materials with a diverging x-ray beam and a transparent substance.

The difficulties of applying the distribution law of particle size are considered and favor is given the law of Gauss' type rather than Maxwellian distribution.

Apparatus for the determination of particle size (5) is discussed by R. Berthold. He considers x-ray tubes, high tension apparatus, and

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(3) M. von Loue; cf. Brill Cd. 23,2360

(4) H. Mark; Trans. Faraday Soc. 25 387 - 9 1929

(5) R. Berthold; Z. Metallkunde 20 378 - 86 1928

universal and multiple diffraction cameras.

Seemann and Schotzky (6) have taken a short time picture with an x-ray oscillograph where the time of exposure equaled one one million two hundred thousandth of a second.

C. Leiss (7) gives a description of a camera for obtaining spectrographs of crystal powder taken on complete cylindrical film.

The original work done in an attempt to use light as an agent for determination of particle size dates back a considerable period. Very little work has been done recently along such lines.

Young (8) observed that when light passed through a set of small holes drilled in a plate that halos were formed around the central hole. Light forms halos on passing through a number of small particles such as water or ice suspended in air as shown by halos formed in clouds. A piece of apparatus was devised to apply this phenomenon to the determination of the size of very small particles.

A metal plate was drilled with a hole .5 mm in diameter. Around this aperture was drilled small holes arranged in a concentric circle about one-half inch in radius. A flame was placed immediately behind the aperture and the plate viewed through the substance under examination. The central hole in the plate was seen to be circumferenced by a halo which could be brought to coincide with the circle of small holes in the plate by moving the substance backward or forward along

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(6) Seemann and Schotzky; Ibid 18 - 85 1930

(7) C. Leiss; Z. Physik 61 663 - 6 1930

(8) Young; Theory of Light, Preston; 3 Ed. by Joly 1901

a graduated scale. The distance between the substance and aperture is read off the scale and this varies inversely as the diameter of the halo. Theory shows that the diameter of the halos produced by different sized particles vary inversely as the diameter of the particles. Thus it follows that the diameter of the particles are directly proportional to the distance between the substance and aperture when the ring appears to coincide with the circle of small holes perforated in the plate. If d be the distance between the plate and substance of radius r when the halo and circle of holes coincide and d_1 and r_1 be similar values for another sample, the following relationship holds.

$$\frac{r}{d} = \frac{r_1}{d_1} \qquad \text{and} \qquad r = \frac{dr_1}{d_1}$$

From this relationship we can calculate the size of particles, provided the apparatus is standardized against particles of known size.

Newton compared the size of particles in milk and other common colloidal materials by this method.

Steman (9) made use of scattered light to determine the size of particles in emulsions and found that the scattering varies as the square of the radius. This indicated true reflection. In many systems the particles can be determined directly.

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(9) Steman; J. Amer. Chem. Soc. 47 1582 - 96 1925

Pohrovshii (10) gives an optic method for determining sizes of particles in suspension. He describes an opaloscope or spectrophotometer for giving the average size of colloidal particles from the scattering of transmitted light.

Of these two general methods for determination of particle size, the x-ray method theoretically should apply to a greater variety of different materials. It could be used with both opaque bodies and translucent suspensions. With this in mind work was first done using x-rays.

The equipment used by Selby (11) was tried out. Voltage varying from 30 to 90 kv. was used but in no case did the radiation appear to be sufficiently intense to register through the plate holder, the sample and then give a pattern on the plate. The tube was found to be defective owing, no doubt, to the inferior vacuum obtained. A faint pattern was photographed using a gas tube to pass rays through a thin film of paraffine on a slide. A glass cell, however, filled with fluffed cotton linters gave no pattern on passing the same x-ray beam through it. This gas tube was very old and cracked when run for long periods.

Owing to the difficulties encountered in producing x-rays, that method was temporarily abandoned and a series of experiments using light was begun. This was patterned after Young's eriometer method. His apparatus was not followed in detail, but varied so that photographic plates could be used to record the size of the spot of light.

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(10) Pohrovshii; Kolloid Z. 47 55 - 58 1929

(11) Selby; Thesis V. P. I. 1932

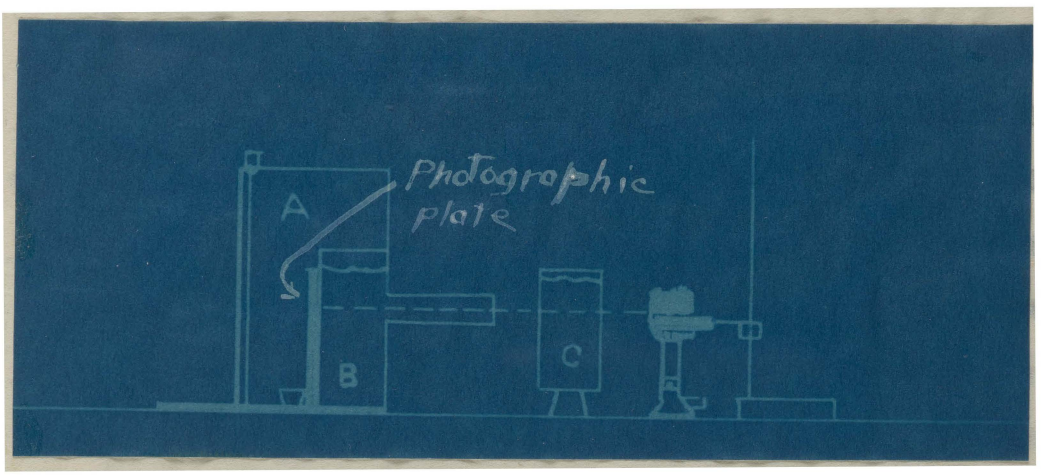
While Young varied his distance from the sample to the plate and kept the size of halo constant, the equations showed that the same effect could be obtained and the same equation apply if the distance was kept constant and the size of the halo allowed to vary. The halo could be measured and the fixed distances for the apparatus determined and then the same calculations made as made by Young. In this work the above set of conditions were held to in that a photographic plate was placed behind the substance to be examined and the halo registered on the plate. After development, the spot was measured and the necessary calculations made.

A small glass cell measuring .6 mm. in inside thickness was filled with a thin suspension of clay. A section of bakelite was bored with a hole .5 mm in diameter to serve as a collimator. A pinhole would give a camera effect while parallel light would give no divergency without colloidal or similar particles.

The photographic plate was placed several centimeters from the cell and the parallel rays of a 500 watt electric light passed through the hole in the bakelith. The light was made parallel by means of two lenses placed in a blackened tube before passing through the bakelite. This set up did not give satisfactory results since there was too much enlargement of the beam for the thickness of solution the light passed through. The light also varied with the focusing of the image on the opening and such an image gave an uneven pattern.

Since much greater depth of solution was found necessary, a water cell four in diameter and 4.5 cms. in thickness and to obtain parallel light a tube .6 cms. in diameter blackened inside and out was used as a light collimator. This was fastened in a blackened

box as shown in the accompaning diagram.



The tube fitted close up against the glass wall of the cell. The photographic plate was placed next to the other side of the cell so that the spot on the plate was the same size as the cone of light on leaving the cell. This differed from the previous run in which the light continued to spread out after leaving the cell until it reached the plate.

A dilute suspension was placed in the cell and light projected into the tube. Several plates were taken but the illumination was still unsatisfactory. Most of the trouble was apparently caused by the electric light and the image of the filament. It was hoped that this unevenness could be remedied by photographing from above the cone of light as it passed through the cell. This was tried by placing a photographic plate on top of the cell just above the beam. It was found however, that a camera would be needed to get this picture.

Because it seemed unsuitable the electric light was abandoned, and a sodium light with a potassium dichromate filter substituted.

Such light is much more uniform and being nearly monochromatic also offers better chance of obtaining sharp borders to the spot in as much as light of each wavelength being diffracted by different amounts would cause haziness when white light is used. The light source finally chosen was a Fisher burner mounted in front of the collimator tube in the flame of which a piece of asbestos saturated with salt solution was suspended. This gave a bright yellow light, uniform in intensity even with slight differences of gas flow.

The intensity of the light was tested by the density of the spot formed in a given time on a photographic plate. The plate was placed against the empty cell and the apparatus closed. A small felt cover was placed over the collimator tube to exclude light. After the flame had burned a minute or too for the light to reach its maximum intensity, the tube was uncovered and the plate exposed for fifteen seconds. The flame was turned out and the plate removed and developed for exactly twelve minutes. This, as well as all other handling of the unexposed plate, was done in a totally darkened room. Another plate was placed in the box and the flame relighted. This time it was adjusted so as not to burn with quite as large a flame as before. The plate was exposed and developed, taking special care that the two time intervals were the same as before.

Special precaution must be taken to get the tube in line so that the flame may shine directly and with full intensity in the

tube. This adjustment is best made before the cell is put in the box. Looking through the back of the box through the tube, the flame is centered and therefore if nothing is moved, each plate will have the same relative amount of light.

The depth of the spots was compared by two methods; by a colorimeter and by the eye. The plates were cut so that the full diameter was close enough to the edge so the plate could be moved back and forth just above the mirrow and under the stage of the colorimeter. A dark solution was placed in the cells of the colorimeter and the outside unexposed section of the plate balanced against the solution. The plate was then moved so the center of the spot came toward the line of view. When the first deepening of color, as indicated by a difference in intensity of light in the two sections of the colorimeter, was noticed; a spot was made through the center of the hole onto the plate. This was repeated on the opsite side of the diameter. The distance from one spot to the other indicates the exact length of the diameter of the spot. It was necessary to mask the full hole under the cells by placing circles of black paper punched with smaller circular holes. This made the location of the spot where the darkening was first observed much simpler.

A method where the size of the spot was obtained using the eye was much more satisfactory. With this method more average values for the sizes were obtained for spots that were not quite round. The plate was laid face down on a piece of white paper. This brought out the border in such a manner that the edge could be easily pick-

ed out with the eye. The readings obtained by this method did not differ by more than 1 mm. This way readings were taken all around the plate while with the colorimeter the reading parallel to the cut edge of the plate was the only diameter obtained so does not represent an average value. This visual method was used for measuring all the plates photographed for the series.

There were four series of plates made. Wyoming bentonite was used to get eight readings corresponding to settling time from 20 minutes to 179 hours. Georgia kaolin, Virginia kaolin and ground flint were used for series of four readings each.

The clays were weighed out in ten gram samples and thoroughly mixed up with water to work up the plasticity and facilitate slaking. This clay was placed in a liter cylinder and made up to volume with distilled water. After being completely mixed by shaking, the suspension was allowed to settle and 50 ccs. samples were pipetted off from the upper layer at the time indicated in the tables below. As shown, the time of settling was measured from the start and not differentially. The 50 cc. samples were placed in small beakers as collected and kept until ready to be photographed. The water used in all suspensions must be perfectly free of electrolytes which would cause flocculation.

The first sample was placed in the cell marked A in the diagram on page 7. To this enough water was added to make a volume of 550 ccs. and the whole throughly mixed. The cell was placed in the box and a circle of black paper pasted on the side of the

cell next to the plate in such a manner that the central beam of light passing through was almost covered. This reduced to a minumum excess reflections. An Eastman panchromatic photographic plate was placed against the back of the cell with the emulsion side in. A weight placed against the plate held it in position. A plate holder slide which had been fixed to the back of the box as a movable door was then drawn down and the plate was ready to be exposed.

The Fisher burner was placed 1 inch from the felt covered collimator tube and the asbestos paper which had been soaked in salt solution was placed in the flame in such a manner that a wall of flame passed up past the tube. When the flame was burning brightly, the felt cover was removed for 120 seconds and then replaced. The flame was extinguished, the plate removed and placed in the developer at 27° C. for 12 minutes. After 20 minutes fixing in hypo, it was washed and allowed to dry.

The diameter of the spot was measured visually. The plate was placed face down on a sheet of white paper and the light arranged so as to come down from directly over the plate. A ruler was used to measure several different diameters of the spot and the average value was taken.

Each 50 cc. sample that was pipetted off was run in this manner. A blank was run by filling the cell with distilled water. The results of these determinations are listed in the table below.

Name of Clay	Sample Number	Time of Settling	Size of Spot Cms.	Average Size	Plasticity (relative)	Slaking Time	Drying Shrinkage %	Firing Shrinkage %
Wyoming Bentonite	A	20 min.	7.75 8.0	7.9	10	10 min.	14	9
	B	1 hr.	7.5 7.5	7.5				
	C	2:20	7.15 7.15	7.15				
	D	5:00	7.00 6.7	6.9				
	E	10:20	7.2 7.4	7.1				
	F	30:20	6.8 6.65	6.7				
	G	70:30	4.4 4.5	4.5				
	H	179:20	4.4 4.4	4.4				
Virginia Bentonite	V_1	40 min.	7.0 7.2	7.1	6	1.5 "	7	13
	V_2	8:10	6.2 6.2	6.2				
	V_3	31:50	5.0 5.2	5.1				
	V_4	120:00	4.5 4.5	4.5				
Georgia Kaolin	G_1 G^1	40 min.	4.6 4.6	4.6	5	3.48 min.	12	11
	G_2	8:10	4.3 4.4	4.35				
	G_3	31:50	4.1 4.2	4.15				
	G_4	120:00	3.9 4.2	4.05				

Name of Clay	Sample Number	Time of Settling	Size of Spot Cms.	Average Size	Plasticity (relative)	Slaking Time	Drying Shrinkage %	Firing Shrinkage %
Ground Flint	S_1	40 min.	7.0 7.3	7.15	.5	30 sec.	1	1
	S_2	8:10 hrs.	6.5 6.7	6.6				
	S_3	31:50	5.0 5.2	5.1				
	S_4	120:00	4.6 4.6	4.6				
Distilled Water	Blank		3.9 3.8	3.85				

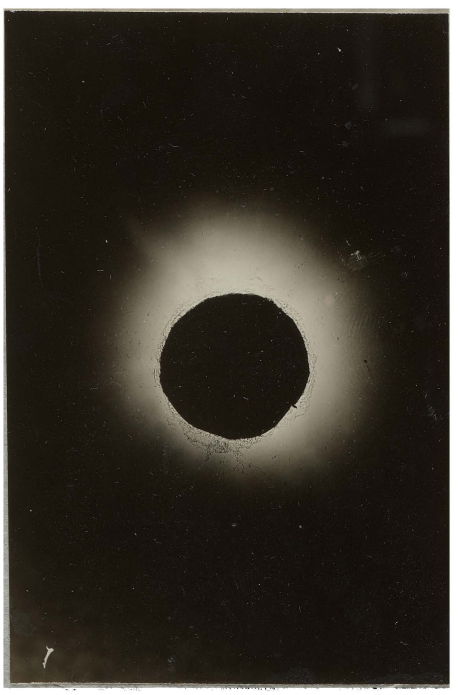
The prints of the plates are included for a permanent record should it be found desirable to make additional measurements of the spots.

G_1

G_2

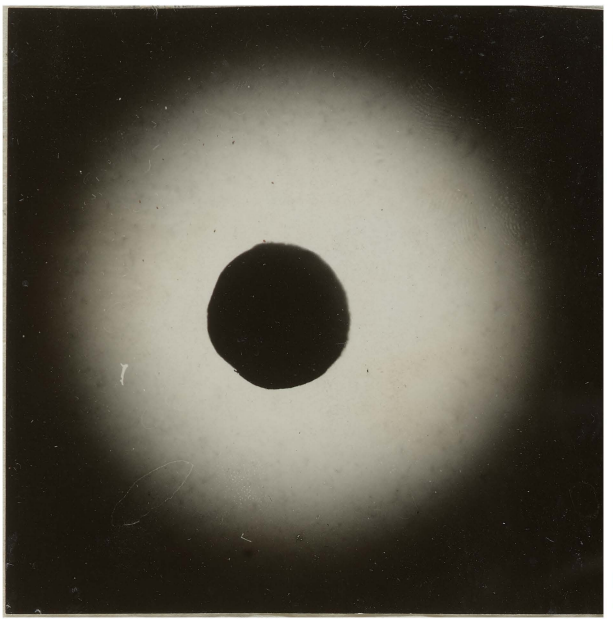
Plate 3

Georgia Kaolin Series

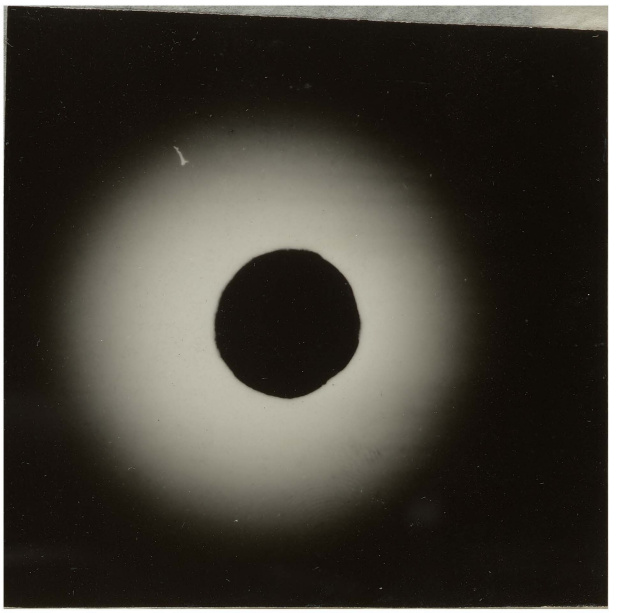


G_3

G_4



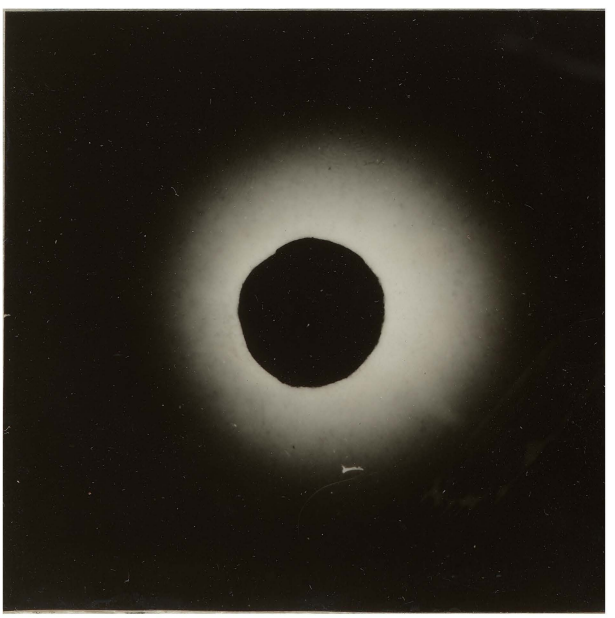
S_1



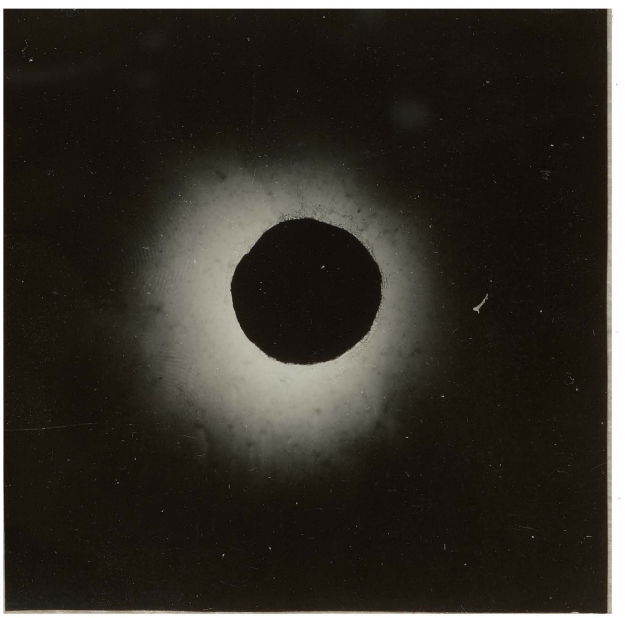
S_2

Plate 4

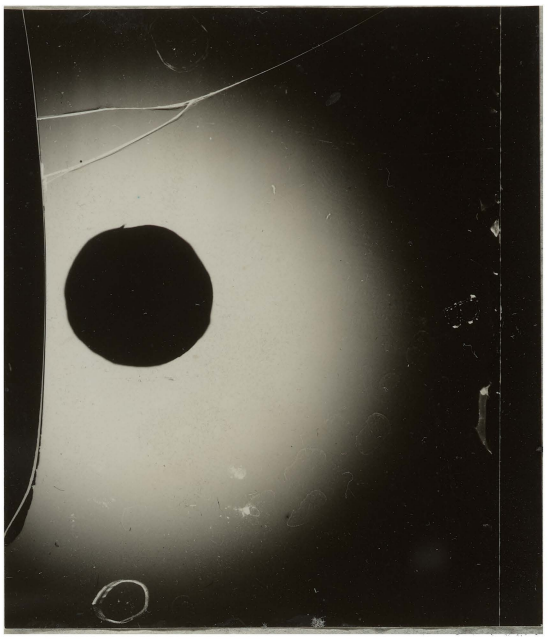
Ground Flint Series



S_3



S_4



A Plate 5 B

Wyoming Bentonite Series

C D

E

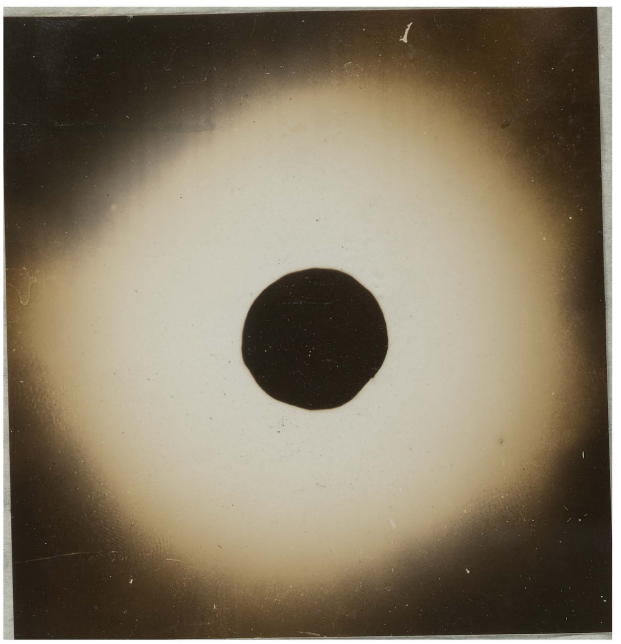
F

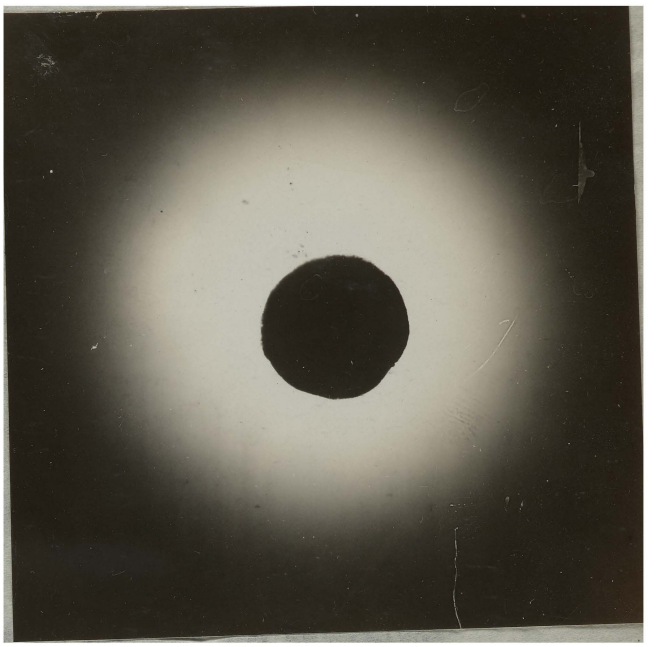
Plate 6

Wyoming Bentonite (continued)

G

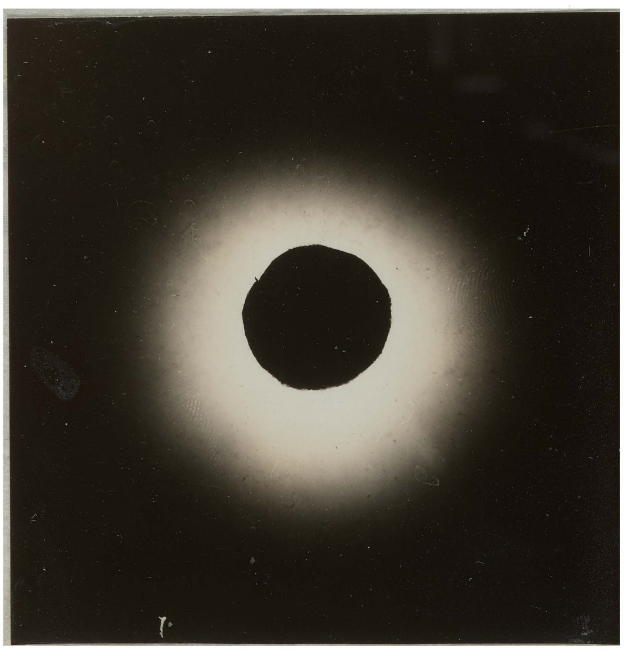
H

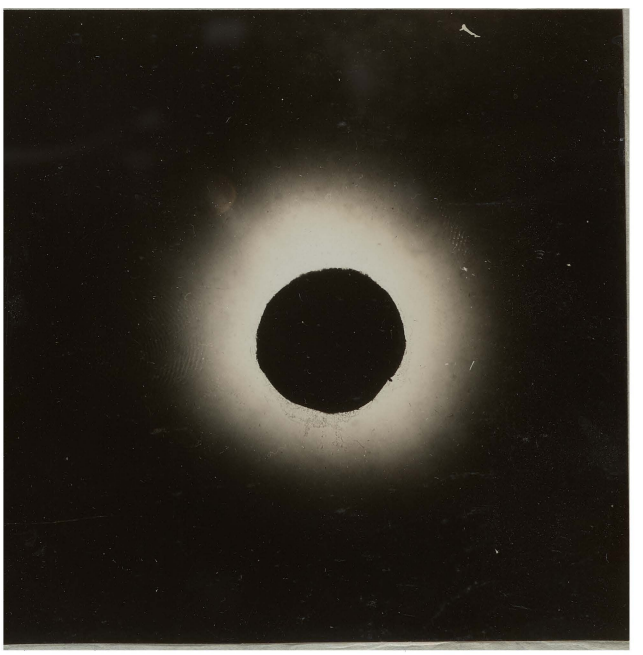




V_1 Plate 8 V_2

Virginia Bentonite Series





V_3 V_4

It may be seen that from this data the relative particle size cannot readily be calculated. With all other influencing factors held constant, the spot should increase in size as the particles of the clay decrease in size. In this case, however, the amount of clay in suspension decreases in amount and tends to decrease the size of the spot faster then the small particles tend to increase the size. For this reason, it was found impossible to apply the equation used by Young to calculate the average particle size.

If a series of graded particles could be obtained and determinations made on weighed samples, the equation should apply. Only the size of particles would vary for the same weight of material could be used in all cases.

A series of curves were plotted with diameter of spot as ordinate and time of settling as abscissa. A second set was made by plotting the size of spot for each clay at the twenty hour period along the ordinate and the corresponding value for plasticity, for slaking time, for drying shrinkage, and for firing shrinkage on the abscissa.

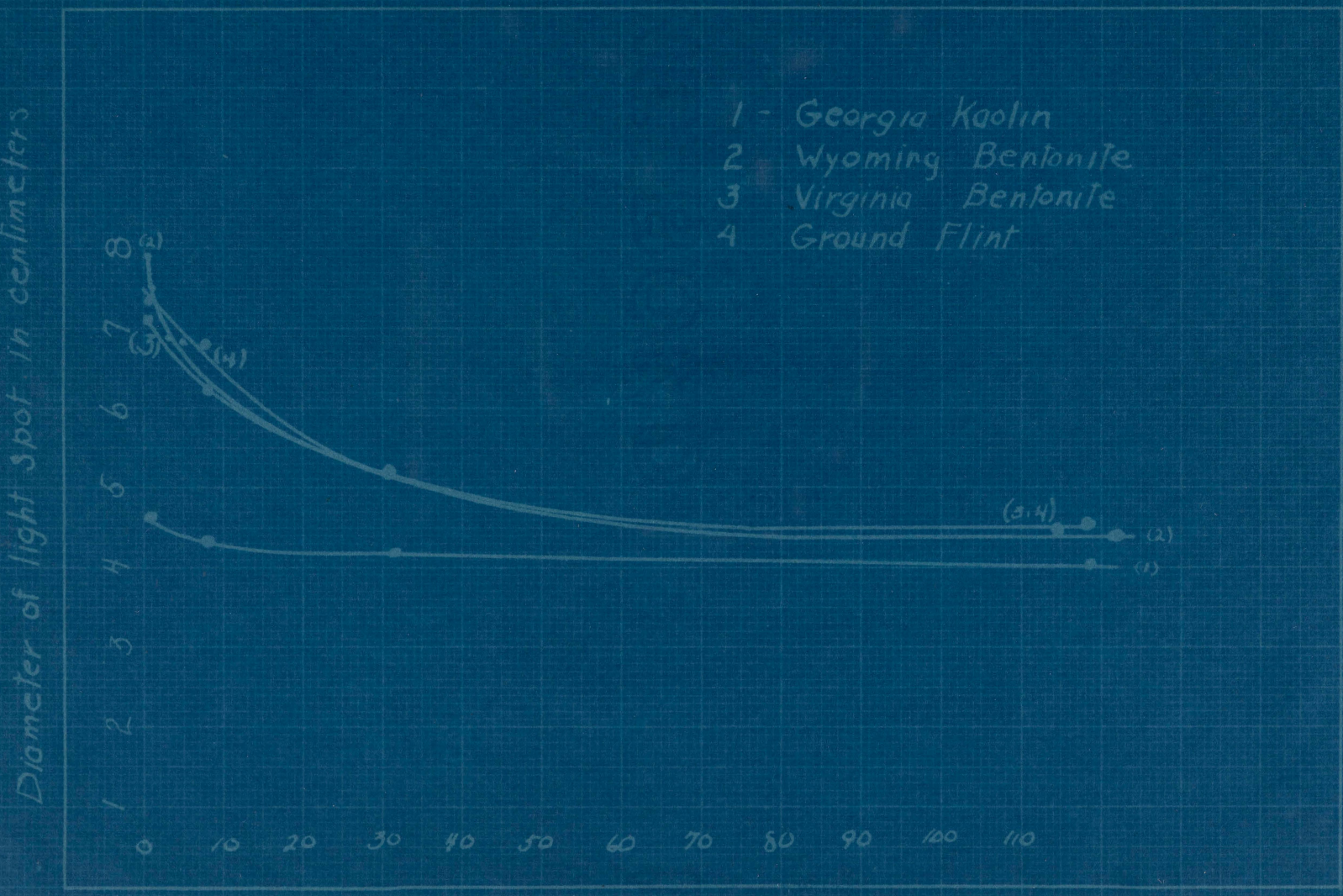
Points and curve #1 is for Georgia Kaolin

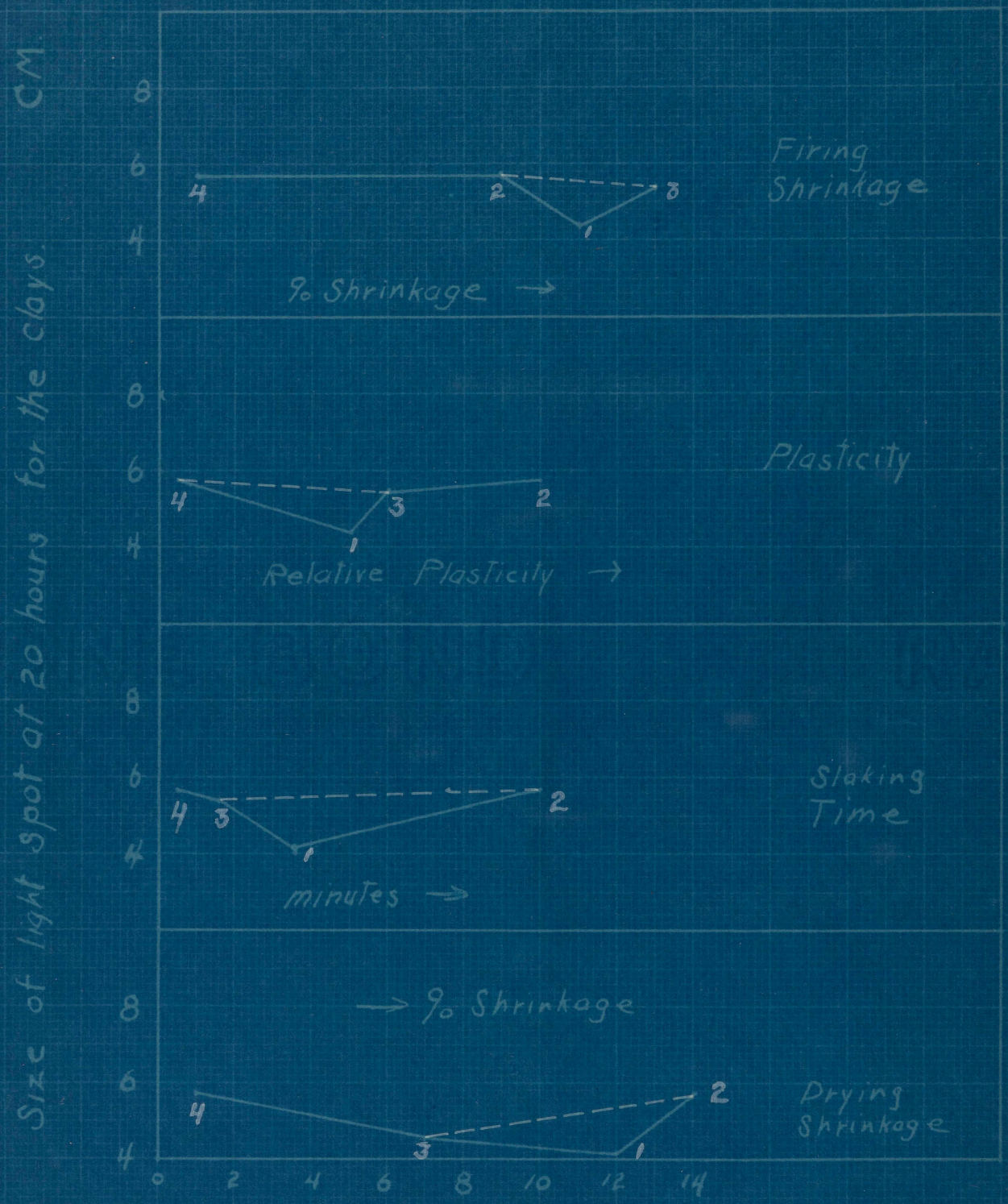
#2 " " Wyoming Bentonite

#3 " " Virginia Bentonite

#4 " " Ground Flint

The results of such plots are shown on the following prints.


1 - Georgia Kaolin
2 Wyoming Bentonite
3 Virginia Bentonite
4 Ground Flint
Diameter of light spot in centimeters
Hours of Settling
0
10
20
30
40
50
60
70
80
90
100
110
1
2
3
4
5
6
7
8
(1)
(2)
(3)
(4)
(3,4)


Size of light spot at 20 hours for the clays. CM.
8
6
4
4
2
3
1
% Shrinkage →
Firing Shrinkage
8
6
4
4
3
2
1
Relative Plasticity →
Plasticity
8
6
4
4
3
2
1
minutes →
Slaking Time
→ % Shrinkage
8
6
4
4
3
2
1
0
2
4
6
8
10
12
14
Drying Shrinkage

Although these plots are not complete, they indicate roughly some relationship between particle size and the properties of the clays, if the Georgia Kaolin be omitted. The dotted lines show the results if this clay is omitted.

It is seen that there is quite a rapid drop during the first few hours of settling but all curves come finally to a constant value. Some effect, such as the Brownian Movement holds the clay left in suspension without further settling for an indefinite time. This amount of material is different for each clay and depends on the size of the particles.

It is suggested that this experiment be tried using clays of which more of the important physical properties are known. The light source should be arranged so that it could be made more adjustable and could be tested each time for intensity. If the samples after being photographed were evaporated to dryness and weighed, the weight of clay present could be plotted against the time of settling and a method obtained for determining the weight of material present at any time or for any size spot. This change, with one by which a change in the size of the spot would be measured instead of the absolute size, should eliminate the chief difficulties met in the work.