

THE JOURNAL

OF THE

American Chemical Society

THE PLASTICITY OF CLAYS.¹

BY FRANK F. GROUT.

Received June 20, 1905.

THIS paper contains a method for measuring plasticity, numerically; the results of a series of experiments on the causes of plasticity followed by some observations on the condition of material in a plastic clay; and the conclusions reached. The work has been conducted in connection with the laboratory work of the West Virginia Geological Survey, in preparation of their Volume III, and it is a pleasure here to acknowledge the kindness which has made the investigation possible, as well as the valuable suggestions received from Dr. G. P. Grimsley, Assistant State Geologist, and other members of the Survey, and Dr. J. L. Sheldon of the Experiment Station.

The experimental data on the subject are meagre, and subject to criticism in the matter of the determination of plasticity. As stated by A. S. Cushman:² "There is unfortunately no better test for plasticity than the simple feel of the clay mixture." This injures all results thus far recorded, from the undeniable fact that one is likely to see or feel what he expects and hopes for. In view of the disagreement prevailing among clay workers, not only in the determination, but also in the definition of plasticity, these were the first points to be settled.

Definition: *Plasticity is the property developed in a clay by*

¹ Published by permission of Dr. I. C. White, director of W. Va. Geol. Survey.

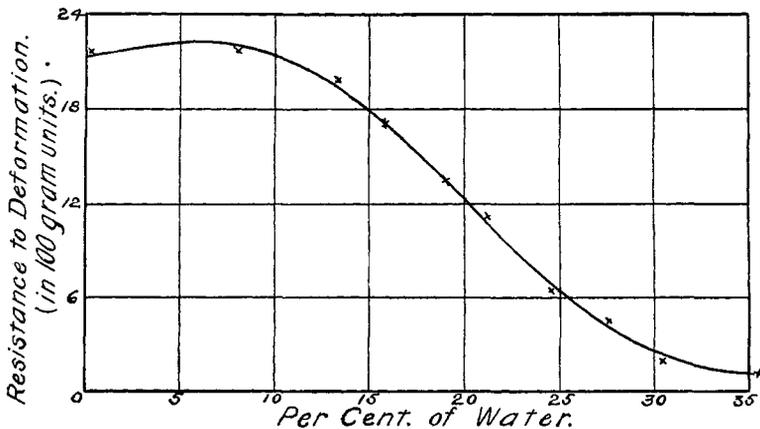
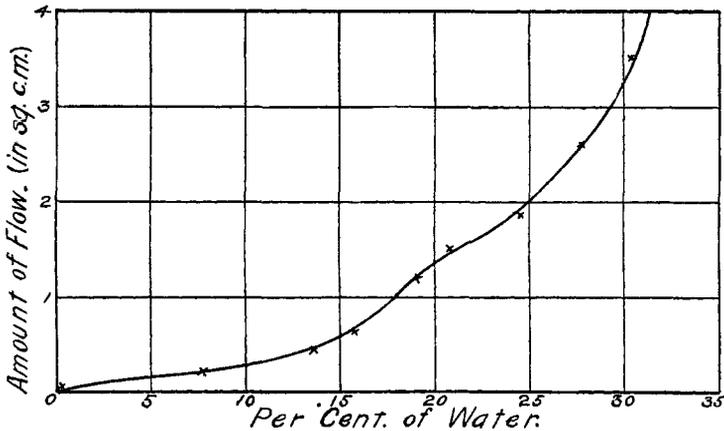
² *Trans. Am. Ceramic Soc.*, 6.

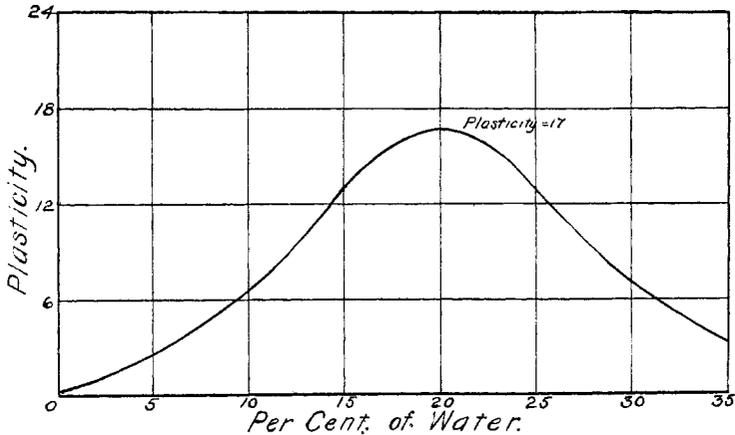
water, by virtue of which it can be molded, without crumbling, into forms which remain stiff and unchanged after the removal of the molding force. It is thus a double property, involving strength and amount of deformation possible before crumbling. The methods of determination heretofore suggested, have invariably neglected the second of these properties, and in some cases based the determination on some assumed relation between plasticity and other quite distinct properties. The use of tensile strength or cementing power of dried clay is an instance of the latter mistake. Its inaccuracy is shown by any extensive series of tests.¹ As examples of methods, which neglect the amount of possible deformation before crumbling, we have Bischof's method of forcing the moist clay through a die and measuring the distance it would project,—Dr. Ladd's measurement of the tensile strength of wet clay and Langenbeck's use of the Vicat needle.

Experimentally, I have tried the simplest possible methods for each of these factors. Tests of compression and penetration were selected as more practical than tensile tests; the handling of unburned clay wares subjects them more often to compression than to tension. Various clays were ground to 40-mesh, tempered, and molded or cut into a variety of shapes. These were compressed and the effects noted. Cylinders were found to give the most uniform results and were easily produced of uniform texture, by tempering one hour, carefully mixing, forcing the mass into a thin walled metal cylinder 2 cm. in diameter, forcing out with a plunger, and cutting into 5 cm. lengths. To obtain the two factors, I recorded first, the weight necessary to compress the upright cylinder 1 cm., and second, the increase in area of the head of the cylinder when the cylinder was compressed to the point of fracture. This area was calculated from the amount of vertical compression, although, of course, the cylinder walls did not remain vertical as implied in the calculation. The fracture occurred as a number of cracks at about 45° to the direction of pressure. The appearance of the compressed cylinder is well shown in Fig. 8, Plate II, U. S. Geol. Survey, Bull. 241, "On Schistosity and Slaty Cleavage," by G. F. Becker. As the method was so simple, a number of readings were taken and the average values were used. It was found that the readings for strength (the weight required to compress the cylinder) varied much more than was

¹ G. E. Ladd: *Georgia Geol. Survey*, Bull. 6-A, p. 32; H. Ries: *Maryland Geol. Survey*, 4, 252 and 260.

desired, and this part of the determination was abandoned in favor of the Vicat needle. As the moist clay exerts considerable friction on the sides of the needle I used a needle of 7 sq. cm. section, so that friction would represent a smaller part of the total reading. As finally selected, the method is as follows: Strength was measured by the weight (in 100 gram units) required to force the needle 3 cm. into a mass of clay 4 cm. deep in half a minute. The amount of possible flow was measured by the increase in area of the cylinder as described above. The product of the two was considered the measure of plasticity at that stage of wetness. But, as the clay dried out, each factor varied in a smooth curve, and the product rose to a well-defined





EXPLANATION OF FIGURES.—The curves for Amount of Flow and for Resistance to Deformation are plotted from experimental data. Then the plasticity of the clay at any certain per cent. of water is found by multiplying the two readings for that per cent. The curve drawn through all such products shows the maximum plasticity of the clay. In this case it is about 17.

maximum at a definite per cent. of water. It was easily possible to measure these values at intervals as the clay dried, and plot curves, and from them, the curve for the product (see diagrams).¹ It is possible, in application of this method, to measure about 16 clays in an eight-hour day. Results range from 1 to 30 for lean and plastic material, respectively.

The following hypotheses have been advanced as causes of plasticity:

(1) *Fineness*.—Proved to be insufficient.²

(2) *Shape of Grain*.—Thin plates. This seems to be quite extensively credited,³ but accurate results are hard to obtain, when the plates are less than 0.001 mm. in diameter.

(3) *Colloids*.—These have been stated definitely⁴ to be capable of improving plasticity, but vital objections can be raised, as will be shown later.

(4) Various other theories are easily shown to be inapplicable.

¹ A study of various curves for plasticity revealed the interesting fact that clays undoubtedly vary in the *quality* as well as in the *maximum amount* of their plasticity, some having a sharp maximum, others a broad rounded curve.

² Beyer and Williams : *Iowa Geol. Survey*, 16, 91.

³ H. Ries : *New Jersey Geol. Survey*, 6, 82 ; E. R. Buckley : *Wis. Geol. Nat. Hist. Survey*, Bull. VI, p. 25 ; H. A. Wheeler : *Ann. Rep. Mo. Geol. Survey*, 1896, p. 106.

⁴ A. S. Cushman : *Trans. Am. Ceramic Soc.*, 6.

EXPERIMENTAL.

The following experiments give a general idea of our results:

(1) *Fineness*.—Shale No. 63 at 40-mesh had a plasticity of 14. At this time about 50 per cent. of it was fine enough to pass a 100-mesh sieve. A duplicate was ground to pass 100-mesh, when the plasticity was 18. Shale No. 64 rose from 3 to 7 by similar treatment. Shale No. 40 gave the reverse result, dropping from 18 to 16. This was unexpected but has been found true in other cases. The majority improve, some are unchanged, and a few are injured a trifle.

It has been shown¹ that addition of sand injures plasticity directly as the diameter of grains increases. Clay No. 16 had a plasticity of 17; mixed with an equal weight of sand at 40-mesh the figure was 7; with sand at 100-mesh, 9. Several shales were only slightly affected by 25 per cent. sand, while others were seriously injured. This was probably due to the presence of some sand in the original clay, so that a small addition brought the total sand to a high per cent. The grinding of minerals not considered plastic gave the following figures:

Quartz at 100-mesh.....	2—.
Calcite at 100-mesh.....	3+.
Muscovite at 100-mesh.....	4+.

These figures are in excess of those obtained by our regular method applied to some flint clays.

(2) *Shape of Grain*.—The above experiment with powdered minerals is full of meaning in this connection. Microscopic work revealed the presence of abundant plates in many clays, but no definite results can be stated.

(3) *Colloids*.—Under this head we may discuss the effects of weathering (though the relation to colloids is doubtful), and the effects of adding colloids to clay; incidentally, also, the staining of colloids, their strength when dry, and power of hydration.

All clays, tested thus far, improve in plasticity by a few days alternate wetting and drying. Weathered river clays show very little change compared with shales. The extreme case was shale No. 64, which rose from 2.6 to 14 in two weeks. Air-drying did not destroy the improvement. The shales ground to 40-mesh weathered to approximately the same figure as the duplicates at 100-mesh. This suggested that the action might be largely mechanical. The

¹ Beyer and Williams: *Iowa Geol. Survey*, 16, 86.

amounts of clay (below 0.005 mm.) in shale No. 63 were determined before and after weathering. The per cent. rose from 7.7 to 17.8 by one wetting and drying. Shale No. 63 was also used to test the action of bacteria. One of three samples of a clay was sterilized with chloroform in a bottle plugged with cotton. The chloroform was removed by thorough evaporation under diminished pressure. Sterile water was used in weathering and great care was taken to prevent any addition of bacteria. The second sample was weathered with city water (Monongahela River), and dried in open air. The third was kept dry. In a week they were tested.

Sterile weathered shale, plasticity.....	18
Ordinary weathered shale, plasticity ...	18
Unweathered shale, plasticity.....	14

It is certain, however, that bacteria can live in clay, and probably do add protoplasm to it; hence, organic colloids, which may increase plasticity in some cases. So much emphasis has been placed on weathering, in the discussion of colloids, that further light was sought, in the determination of combined water before and after weathering. After two weeks' weathering and large increase of plasticity, three samples were air-dried for twenty-four hours. Hygroscopic moisture varied from the original, some increasing, some decreasing. But when calculated to 100 per cent. without this free water, the combined water checked very closely with the original unweathered clay (0.02 per cent.). The amount of combined water in a clay does not change with rise of plasticity. An increase was noted in the soluble salts. Possibly the sulphides were oxidized, or the mechanical action exposed more surface to the solvent.

Two experiments will illustrate our results in adding colloids to clay. Two distinct types of substances were used, colloidal solutions and gelatinous precipitates. A very dilute solution of the agar-agar of bacteriologists was used instead of water in tempering two clays of plasticity equal to 7 and 11. The figures were increased to 11 and 15 respectively, by as small an addition of agar as 0.08 per cent. of the weight of the clay. The addition of 0.2 per cent. caused a further increase, but not in proportion to the amount added. Now one of the great objections to the colloid theory¹ is "the very small and inconsiderable proportion

¹ Beyer and Williams : *Iowa Geol. Survey*, 16, 90.

of ingredients which are capable of assuming the colloid state by the action of water alone." It will be noticed that 0.2 per cent. is an inconsiderable amount which produces an effect well worth considering. Further, agar has a gelatinizing effect ten times as strong as gelatine, another colloid. It is conceivable that some substance may be even more active than agar, so that a few hundredths of a per cent. may increase plasticity remarkably. After the agar was added, the samples were air-dried, gently crushed to 40-mesh, and the plasticity measured. It was as high as when agar was first added. Ten grams of the air-dried samples were heated with water and settled for a determination of the soluble salts. It was supposed that the presence of a colloid would be noted in that determination. *No jelly could be obtained.* To further test for the presence of a soluble colloid the whole sample was washed with hot water on a porcelain filter for two days. Its plasticity was unaffected. The same was true for a plastic clay (No. 16) which had not been treated with agar.

Alumina-cream was washed by decantation and used without drying, instead of tempering water. It required an amount (measured as Al_2O_3) equal to 3 per cent. of the weight of the clay to raise the lean clay (7) as much as 0.08 per cent. agar (11). The mass was then air-dried, powdered, and the plasticity measured. It had dropped to the original figure (7). Weathering a week increased it less than half a point. As plastic clays are not thus injured by air-drying it is evident that such colloids as alumina cream do not explain plasticity. Some colloid is required which will soften in water after air-drying, and these are extremely rare in the inorganic kingdom. The suggestion of some recent writers,¹ that a hydrated silicate of alumina could be precipitated so as to give the desired properties, has been carefully tried, but all resulted exactly as the alumina cream. Most of the silicate was prepared by mixing sodium silicate and alum solutions, both of which are supposed to occur in clays as decomposition products of other minerals. No precipitate was obtained which would appreciably soften after air-drying. The assumption that some unknown silicate of alumina possesses such a property is unjustified by the known properties of inorganic colloids.²

¹ A. S. Cushman: *Trans. Am. Ceramic Soc.*, 6.

² A recent writer ascribes the viscosity of colloids to a physical heterogeneity of the solution. Many authorities find no distinct line between colloidal solutions, colloidal suspensions, and other suspensions. With this in mind it may be said, that the finest

The fact that colloids are stained by methylene-blue has recently been presented in the discussion of colloids.¹ I find that most clays contain from 1 per cent. to 5 per cent. of grains which will take a stain from methylene blue, gentian violet, eosin, or fuchsine. These might be classed as colloids or "pectoids," though their exact nature is undetermined. For, I find much organic matter will take such stains; freshly gelatinized silicic acid will stain easily; *air-dried silicic acid jelly will take the stain with equal readiness*. Now, air-dried silicic acid has an action *identical with angular quartz sand* in affecting plasticity of clay, injuring, instead of causing plasticity. Some clay grains which stained very little showed a border or spot of color, agreeing with the idea that the production of this form, capable of being stained, is due to some secondary action. But weathering, with its remarkable increase in plasticity does not materially increase the number of grains taking the stain, nor the depth of color. The observation of "minute spherical particles, which may be of colloidal character,"² thus loses some importance. The fact that they are amorphous does not necessitate softening in water. In this connection, a recent writer³ has found that high magnification reveals crystalline structure in the "globules" of Zettlitz kaolin, which have long been considered amorphous.

The value of strength tests, in discussing colloids, is indirect. Plastic clays are often strong. Colloids added to a powder, often increase its strength. Hence, it is argued, colloids are in clay. But the conclusion is not inevitable. Colloids, like air-dried silicic acid, *decrease* strength, and in studying the substances which *increase* it, we find that not only colloids like agar but crystalloids like gypsum and alum, are quite active.

The absorption of hygroscopic water is another indirect argument. Clays absorb water. Colloids absorb water. Hence, it is said, clay contains a colloid. But it may be a colloid like dried silicic acid, so that nothing is indicated in connection with plasticity. The colloid structure is admittedly destroyed by ignition, but we have found some thoroughly ignited clays which

clay particles *do* remain suspended indefinitely; they *can* be coagulated like colloids by heat or the addition of salts; possibly they are active in increasing viscosity, and thereby, also plasticity. But this is not the meaning of the colloid theory as it is usually stated.

¹ A. S. Cushman: U. S. Dept. Agr., Bur. of Chem., Bull. 92.

² H. Ries: *New Jersey Geol. Survey*, 6, 83.

³ S. Kasai: *Z. Krist. Min.*, 1899, p. 653.

absorbed water in amounts quite comparable with unignited clay, after standing in moist air.

CONDITION OF A PLASTIC CLAY.

After a little kneading, each grain in a mass of clay is wet on all sides by a film of water. Of course, if the grains are angular and the water is not abundant, or if the pressure is considerable, the adjacent grains may penetrate the film and come in direct contact. But through some force—call it capillarity, or surface tension, or some other¹—the water spreads in films around the grains. The cohesion of water, the adhesion of clay grains and water, and the cohesion of clay through the water films, unite to make the moist clay hang together. At the same time the water films act as lubricants. This combined cohesion and lubrication forms the ultimate basis of plasticity. A simple illustration is the action of two glass plates with water film between. When dry, friction is great and cohesion small, both in case of the ground clay and the glass plates. As water is added friction decreases till no greater than that of the liquid. Cohesion meanwhile becomes large, just as enough water is added to wet the surfaces, and then steadily decreases when excess of water is added.

Plasticity, as defined above, will depend on two factors; first, the *distance* the clay particles can move on each other without losing coherence; and second, the *amount* of that coherence, or the resistance to movement. Under the first factor we find that the distance will vary with (*a*) the shape and size of grains and with (*b*) the distance through the film that they will attract each other. Under the second factor we find the resistance to deformation will depend on (*c*) the friction in the film and (*d*) the friction of the grains on each other, as they become irregular and penetrate the film.

(*a*) It is evident that two plates $2 \times 2 \times \frac{1}{4}$ inches will glide farther without losing coherence than two blocks $1 \times 1 \times 1$ inch, though the bulk is the same. Again, angular grains may cohere, but relatively small movement will cause such a separation, due to the rough surfaces, that coherence becomes inappreciable. Again, two blocks $1 \times 1 \times 1$ inch could be extended into a coherent mass of much greater length if the blocks were subdivided. Fineness also increases the surface exposed, requires more water, and thus improves lubrication.

¹ G. E. Ladd: *Geol. Survey of Georgia*, Bull. 6-A, p. 31.

(b) The attraction of two clay grains may vary, with the nature of the grains. The greater the attraction the farther they can be separated without losing coherence. This will be discussed presently in detail.

(c) The film may produce more friction to gliding in several ways. It may become greater in area. The friction of two plates $2x2x\frac{1}{2}$ would be four times as great as two blocks $1x1x1$. Again the film may become viscous. The action of colloids is probably at this point. Another way in which the films become viscous is the result of molecular attraction, which *binds* a film over the surface of the grain and renders it viscous.¹ The thinnest films are most viscous, and the films attracted most strongly by the grain are most viscous. The friction between this film and the solid grain of clay, is said to be infinite, compared with water outside of the film.² But when forced to move the resistance would depend on the strength of the attraction of clay and liquid.

(d) It is evident that wet rough sandstone will exert more friction than wet polished glass.

Twice in the above summary of the possible variations in a clay I have referred to molecular attraction. This is yet to be justified. The extremely small range of its influence seems to render it insignificant. Quincke finds that glass attracts water in this way for 0.00005 mm. Other men and methods give results of the same order of magnitude, this figure being the one quoted by the text-books. Now a simple calculation, based on the mechanical analyses of clays, will show³ that the amount of water needed, to place a film 0.00005 mm. thick around each grain is

¹ Dr. Ladd (*Ga. Geol. Surv.*, Bull. 6-A) mentions that the "mutual attraction" of clay and water is so great that it gives a certain "rigidity" to the water, thus giving strength to a clay when it is so wet, one would expect it to be quite fluid. But he gives no data to show that this cause is sufficient to produce the results mentioned. In fact, he refers mainly to capillarity (p. 21), whereas, the rigidity is to be found only in the sub-capillary films. He further attributes the "pull" to *chemical composition* (p. 31), which we will consider later. Beyer (*Iowa Geol. Surv.*, 16, 97) also speaks of the physical attraction of particles for the surrounding one through a film of water, but he fails to note the effect on viscosity and the fact that attraction may differ, with different substances.

² Daniell, Alfred: "A Text-book of the Principles of Physics," 3rd Ed., Macmillan Co., p. 306.

³ Our mechanical analyses frequently show a large per cent. of grains below 0.001 mm. in diameter, also from 0.001 to 0.005 mm. The average diameter of grains below 0.001 mm. is 0.0005 mm. If these are considered spherical and of specific gravity 2.5, it would require 25.5 per cent. by weight of water to place around each grain a film 0.00005 mm. thick. If the grains were considered plates one-fifth as thick as wide, instead of spheres, over 54 per cent. of water would be required. Then in an average "fine clay," 40 per cent. of water will produce only sub-capillary films. A similar calculation for the clay from 0.001 to 0.005 mm. in diameter shows that it would require 8 per cent. Thus many of our clays require 25 per cent. of water to produce these films.

often nearly equal to the amount added in tempering. So that in ordinary plastic clay, it is necessary to consider practically all the water as being under this influence. The change in viscosity or in thickness of the film, seems to be beyond the region of experiment. The quantity is too small to admit the determination of slight changes, but such are constantly assumed in physical problems. W. J. A. Bliss,¹ speaks of clay particles and the surrounding adherent liquid, as follows: "*The thickness of this shell depends on the intensity of the attraction between the solid and the liquid.*" J. E. Mills,² says, "*molecular attraction depends primarily on the chemical constitution of the molecule.*" This is the essential fact of our theory. Some hydrous silicate of alumina attracts and holds a thicker film of water in a viscous condition than most powders. Another factor besides the constitution of the solid is the quality of the liquid. Slight amounts of soluble salts in the water will change the attraction. W. J. A. Bliss, in the above-mentioned article, suggests this explanation for the coagulation of suspended clay particles and the reverse effect by other salts.

The molecular constitution on which this theory rests, is not to be confused with composition. Kaolin may or may not be plastic. Amorphous varieties have been appealed to in explaining the variation in kaolin, but this may not be necessary. Dr. F. W. Clarke suggests³ seven possible formulae for crystallized kaolin; two being more probable than others. Our suggestion is that at least *two exist*. Similar changes are suggested⁴ to account for changes in the physical properties of other silicates, *e. g.*, orthoclase

¹ *Phys. Rev.*, 2, 373 (1894-5).

² *J. Phys. Chem.*, 1902, p. 209.

³ In *U. S. Geol. Surv.*, Bull. 125, Dr. Clark recommends the formula $\text{Al} \begin{matrix} \diagup \text{OH} \\ \diagdown (\text{SiO}_4)\text{K}_3 \\ \diagdown (\text{SiO}_4)\text{Al} \end{matrix}$. The

kaolin, however, is a very stable compound, and, as he suggests, the group $-(\text{SiO}_4)\text{H}_3$ is doubtful. The stability also favors a more symmetrical arrangement. In quite an extensive series of tests in our laboratory no difference was found in the ease of extracting the atoms of any one element of the kaolin. Comey's "Dictionary of Solubilities" refers to Malaguti as authority for the extraction of one-fourth of the silica by potassium hydroxide. We could not confirm this. Sulphuric acid, bromine, chlorine and ammonium chloride, if used at a temperature and concentration to attack kaolin, will do so progressively and, in the end, completely. We therefore favor the formula $\text{Si}_2\text{O}_5 \cdot 2\text{Al}(\text{OH})_2$, credited to Groth. The diorthosilicate is also symmetrical, $\text{Si}_2\text{O}_7 \cdot \text{K}_4(\text{AlO})_2$; but the group $\text{Si}_2\text{O}_7 \cdot \text{H}_4=$ should be open to the same objection as the group $-(\text{SiO}_4)\text{H}_3$. Several other complicated symmetrical formulas can be imagined, but the simplest, most symmetrical is the dimetasilicate of Groth's. The trisilicate offers the most evident opportunity for isomeric salts, but does not offer a symmetrical arrangement. This, of course, does not effect the evidence found in the relation of kaolin to other silicates, which led Dr. Clarke to recommend the first formula mentioned.

⁴ Van Hise: *U. S. Geol. Survey*, Mon. XLVII, p. 202.

and microcline. In case of kaolin we may therefore imagine a change in physical properties, due to the chemical constitution of the molecule, but considerable experimental work has not suggested wherein the constitution varied, nor how one might hope to obtain the desired form.

SUMMARY.

(1) Sand injures plasticity little at first because the grains are suspended in a plastic mass. It is only when grains are abundant enough to come in contact with their neighbors, that the effect becomes serious, and then both strength and amount of possible flow are injured.

(2) Certain rare organic colloids increase the plasticity by rendering the water viscous.

(3) Fineness also tends to increase plasticity.

(4) Plane surfaces (plates) increase the amount of possible flow. They also give a chance for lubrication by thinner films, thus increasing the friction of film, and the strength of the whole mass. The action of plates is thus twofold; but fineness may be carried to such an extent as to break up plate-like grains into angular fragments. The beneficial effects of plates are also decreased by the fact that each is so closely surrounded by others in the mass.

(5) Molecular attraction is twofold in increasing plasticity. As the attraction increases, the coherence and strength of the mass increase, and the amount of possible deformation before crumbling also increases. Fineness increases this action by requiring more water. Colloids and crystalloids in solution may also increase the attraction. It is thus seen to be more active than any other single factor.

CONCLUSION.

Molecular attraction depending on the chemical constitution of molecules is the chief cause of the high degree of plasticity found in clays. But practical work in improving clays¹ may well follow the lines already started; first, the addition of such colloids

¹ The tendency for tensile strength to vary with plasticity is also easily explained in this way. Molecular attraction between two kaolin grains may be high. If the attraction for water is high, some water will be drawn between the grains and rendered viscous by the attraction; this makes plasticity high. But when the water dries out from such a mass, the kaolin grains still attract each other, and the chances are for greater strength than when wet, because the water has acted as a lubricant, allowing a readjustment of grains to fill the space left as the water moved out. The result is a high degree of consolidation

as tannin, etc., or such solutions as ammonia, alum, etc., which can be shown by experiment to produce the desired results; and second, weathering, with its mechanical action and its possible addition of colloids by bacteria.

W. VA. GEOLOGICAL SURVEY.

MORGANTOWN, W. VA.

June, 1905.

LIQUID MIXTURES OF MINIMUM BOILING-POINT.

BY C. D. HOLLEY AND J. T. WEAVER.

Received June 10, 1905.

THREE YEARS ago one of us, C. D. Holley,¹ presented the results of an investigation of sixteen pairs of liquids of which amyl alcohol or its derivatives formed one constituent. Of these sixteen pairs, five gave mixtures having well-defined minimum boiling-points, two showed no relative elevation or depression of the boiling-point and the remaining nine presented no unusual phenomena. In this paper the writer reports the results obtained with a series of pairs of liquids with propyl and isobutyl derivatives as one of the constituents, together with some miscellaneous curves. The investigations made with carbon tetrachloride were carried out under the direction of the writer by J. T. Weaver in the North Dakota Agricultural College Laboratory.

The apparatus and methods of procedure were the same as described in the previous article, a Hite's apparatus provided with a thermometer reading to fifths being used. A weighed amount of the lower boiling constituent was introduced into the bulb and boiled for several minutes, the boiling-point and barometric pressure being noted. Weighed amounts of the other constituent were added and the successive boiling-points recorded until the liquids were present in nearly equal proportions. The process was then reversed beginning with the higher boiling constituent.

The liquids used were supposed to be chemically pure as purchased, but before being used were further purified by distillation, the first and last fourths being rejected. The bulb of the Hite apparatus was kept covered and the distillation carried on in subdued light, and it is believed that the bromides underwent very slight, if any, decomposition. From twenty-five to thirty readings were made with each pair of liquids, and as the minimum point was approached the successive portions of the added con-

¹ This Journal, 24, 448 (1902).