STUDIES IN SALT RESISTANT DRILLING MUDS

by

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Submitted in Partial Fulfillment of the Requirements for the degree of

MASTER OF SCIENCE

From the

Massachusetts Institute of Technology

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Signature of Author

Department of Geology, May 22, 1941

Signature of Professor in Charge of Research

Signature of Chairman of Department Committee on Graduate Students

216267
Massachusetts Institute
of Technology
Cambridge, Massachusetts
May 22, 1941

Prof. George W. Swett
Secretary of the Faculty
Massachusetts Inst. of Technology

Dear Sir:

I am submitting herewith in accordance with the requirements of the faculty a thesis in partial fulfillment of the requirements for the degree of Master of Science in Geology.

Yours very truly,

Louise I. Houssière
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OBJECT

The object of this work was to try to reduce the effect of electrolytes on a drilling mud. To try to accomplish this end, the dispersing agent "Daxad" was used.

To date, there has been no available literature which might give some suggestion as to how this problem might be solved.
INTRODUCTION

Oil well drilling muds are made up largely of clays or from shales and mudstones which have the power of disintegrating in water to form clayey masses. These clays are composed mainly of alumino silicic acids in which a certain proportion of the hydrogen has been replaced by sodium or other elements. (See Appendix) No definitely satisfactory hypothesis has been as yet produced to account for the peculiar properties which are displayed by these clays but their properties are generally attributed to the presence of extremely minute particles which form platy or fibrous structures. In addition to the natural clay other substances may be added in preparation of the fluid. These substances may include colloid materials which improve the quality of the mud if inferior clays have been used; heavy minerals such as barytes and iron oxides which add to the weight of the mud; and chemicals such as tannins and pyrophosphates which reduce the viscosity of the mud.

The drilling mud so prepared is sent down by means of a pump into a vertical, hollow, cylindrical pipe, which is rotated by a mechanism above the
The hollow pipe has on its end (see Fig. 1 in the Appendix) a bit in which are found holes. The mud is forced out of the openings as the bit (labeled "2" in Fig. 1) rotates, travels the small distance to the bottom of the hole ("3") and is forced up the annular space ("4") between the hole and the pipe. Upon reaching the surface it is allowed to settle in various pits of special design or it may be passed over a "shale shaker". Both these alternatives serve the purpose of releasing the cuttings from the mud before it begins its circulatory trip down the hole again.

Mud fluids as used today in the petroleum industry fulfill many purposes. Some of these purposes are: to plaster or build up the walls of the hole; to cool and lubricate the bit; to remove the cuttings; to prevent "blowouts"; and to keep the cuttings in suspension when drilling operations are suspended.

The mechanism of building the walls of the hole in rotary drilling is a purely mechanical process of "bridging" the pores of the formation by suspended solids which are in the mud. It is desired
to bridge these openings so that water may not find its way into the formation to bring about "caving"; and so that the passage of ions in the formation which might "floc" the mud and destroy its other properties as well is prevented. To accomplish this bridging satisfactorily there must be present in the mud both large and small particles so that the pore openings may be adequately closed. If these various sized particles do not occur naturally in the mud they may be added in the form of a highly colloidal clay such as bentonite or they may result from a chemical deflocculation or dispersion of clays already present by the addition of dispersing agents. For good wall-building properties not only an abundance of these particles is necessary but they must be in a state of deflocculation - otherwise, their effective size will have been increased and the distance between them and the molecules of water will have increased and the latter will be able to penetrate into the formation.

The cooling and the lubrication of the drilling bit by the mud is brought about by the removal of heat generated in drilling and by enabling the bit to cut into the formations with greater ease.
The cuttings which are removed are produced as the bit breaks up the formation and they must be removed at once in order that the bit may continue its work. They are removed by the upward action of the mud. The ability to remove the cuttings effectively depends on the viscosity, the density, and the rate at which the mud flows. The density is what is commonly known as the "weight of the mud". Although the standard unit of density is "pounds per square inch per 100 feet of depth" according to the American Petroleum Institute, such terminology as "pounds per cubic foot" or "pounds per gallon" is also used. The density of the mud must be great enough so that blow-outs are prevented. Viscosity, which is a measurement of the internal resistance of a fluid to flow (the greater resistance correlating with greater viscosity) must be controlled so that upon reaching the surface the cuttings may be easily removed, the entrained gas may expand and be released and excessive pump pressures may be avoided. If the viscosity is not controlled, in the case of a very viscous mud, opposite effects may result. In addition to the possible "opposite" effects, a swabbing effect may be created
when the drill stem is removed from the borehole and the mud level in the hole will be reduced; the hydrostatic head on the porous formations may be reduced; other serious difficulties may follow.

In removing the cuttings from the well a story of the geology through which the bit is passing is told. Trained people in the field of "well-cuttings" are able to tell with very little hesitation exactly what formations are being penetrated from the particles of rock which are brought up to the surface. The attachment of an automatic alarm in the mudstream enables the operator to detect minute quantities of gas and at times it has proved to be so effective that operators have been warned of the presence of gas fifteen to twenty feet before the formation which contained it was actually penetrated. To detect the presence of oil in the mud, use is made of ultraviolet light and quantities as small as one part of oil to one hundred thousand parts of mud have been detected. The salt content in the mud may be measured by placing electrodes at the "in" and "out" streams of the mud which measure the resistance of both.
The mud must be able to suspend the cuttings which it contains in the hole when drilling operations are stopped so that the cuttings will not accumulate (cake) at the bottom of the hole and cause the bit to "freeze". The ability of the mud to do this depends on its thixotropic characteristics. "Thixotropy" may be defined as an adiabatic sol-gel transformation or as the property which a sol possesses to gel when at rest and becomes liquid again when it is agitated. It is explained as the condition which exists when there is a perfect balance of the attractive and repulsive forces between adjacent particles in a dispersion.

The changes which occur in the thixotropy of a mud when variations in concentration of electrolytes are encountered in the hole present one of the major problems today in the field according to most drillers. Since a mud of normal field consistency can only exhibit the property of thixotropy when an electrolyte has been added within a certain range of concentration, increasing the concentration of electrolyte will bring about flocculation or the formation of an "irreversible coagulum". This "floc" may
no longer be redispersed and the mud can no longer be used.

It was because of the ease with which drilling fluids are coagulated that this problem was undertaken. The coagulation is brought about by the interaction of the negatively charged clay particles and the positively charged cation of the electrolytes which are encountered while drilling. The charge which the negative ion of the electrolyte possesses also plays an important role. The colloidal clay particles possess a negative charge as a result of substitution of some of the ions in the layer-like lattice of the bentonite (see Appendix) by ions which have a smaller valency, a residual net negative charge resulting.

When the clay particles are dispersed in water, the cations which are adsorbed on to the layer lattice to satisfy the residual charge dissociate out into the medium, being restrained from escaping by the electrostatic forces of the particle. This dissociation causes the clay particle to swell. As more electrolytes come into contact with the particles, they may continue to charge the particle until
a maximum charge is reached. From this point more addition of electrolyte will tend to decrease the diffuse outer layer of the colloid micelle (See Appendix) discharging the particles, the outer layer of the particle decreasing to such an extent that the kinetic energy of the molecules may bring adjacent particles together as they come closer to each other. This results in coagulation. As has been shown, coagulated particles can not play a very important in the role of a drilling mud because they can not display good wall-building properties, they can not maintain their thixotropic effect, and they can not remove the cuttings effectively.

Primarily, negative tests were used to reduce the effect of electrolytes. For many years the practice was to drill until salt was encountered with the hope that oil would be struck before that occurred.

Positive methods which have been utilized to try to reduce the action of salts have been varied and none have been very successful. The addition of protective hydrophilic colloids which have the power of being "adsorbed" on to the clay particle
and which are not in themselves very readily attacked by electrolytes have been used. A disadvantage to their use, however, other than their expense (in some cases) is that if too large quantities of them are added, the system will not gel, and their purpose is defeated. Recent research by one of the major oil companies which has carried its results into the field has shown that particles in the mud to which has been added starch (a protective colloid) can "stand up" under the influence of electrolytes because their charge is "protected" by the starch which surrounds them. The company maintains that in their drilling operations that it has been actually possible to penetrate salt beds in several tests. Furthermore, no complaint is made about the wall-building properties. However, these tests have been carried out on relatively shallow wells and whether or not the starch would be able to perform the same work under extreme pressures and temperatures which are encountered in deeper wells is speculation. Viscosity reducers such as tannins and pyrophosphates have been experimented with but as is found in the case of many of the protective colloids, the expense
of these chemicals has not as yet been found to warrant their use, to any great extent. A technique of prior saturation of the mud with salt to prevent further dissolving of the salt in the formation has actually been tried in the field but because of the very poor wall-building property of the flocculated mud it can not be advantageously used.

With these attempts in mind it was decided to study the effect of dispersing agents on such a system. The dispersing agents under consideration were Daxads. "Daxad" is the generic term used to apply to various polymerized organic salts of sulphonylic acid of the alkyl-aryl type. Daxad 11 is the condensation product of formaldehyde and naphthalene sulphonylic acid; Daxad 21 is the Na salt of naphthalene sulphonylic acid; and Daxad 23 is the Ca salt of naphthalene sulphonylic acid. (See Appendix) The action of these dispersing agents is not as yet completely understood but it is believed that they put like charges on the individual particles which are then able to repel each other and in doing so reduce the cohesive forces between the
primary particles of the clay, breaking up flocs and agglomerates and making each particle act as an entity. In doing so, these dispersing agents aid in the production of very fine dispersions. They have no pronounced surface activity and therefore can not be classified as wetting agents. Many substances possess individual limits of comminution possible through grinding in the absence of dispersing agents and may be found to mechanically reaggregate unless such a dispersing agent is present to increase its active surface and thereby increase its fluidity when placed in contact with water. With such an increase in the number of particles and the increased charge it seems to follow logically that it would be necessary to have a larger quantity of electrolyte present to coagulate the same amount of material than it would have originally.

The effect of Daxads on the following clays was studied: Aqua Gel, Spudmud, Boganite, Tennessee No.7 Ball, Tennessee No.1 SGP, Black Monroe Wad, Grun-dite, and K.T.Ivory. (For analyses, see Appendix)
PROCEDURE

In order to arrive as closely as possible to the size of particles ordinarily employed in drilling muds, those clays which contained large lumps were ball-milled for a period of twenty-four hours. Clays to which this primary ball milling was applied were: Tennessee No. 1 SGP, Tennessee No. 7, Black Wad Monroe, Grundite, and K.T. Ivory. Aqua Gel, Boganite, and Spudmud were considered to be finely enough divided. The ball-milling was carried out in heavy crocks which were filled about two thirds full with pebbles and clay, the ratio of pebbles which were to serve as the grinding agent to clay was about two to one. No water was used in the milling operation.

It was decided to combine the Daxads with the clay in three combinations to find out which combination gave the best results. In all cases, the ratio of one gram of Daxad to one hundred grams of clay was maintained. In making up solutions, ordinary tap water was used in order to try to simulate as nearly as possible conditions found in the field. The combinations of Daxads used were:
a. Each Daxad used, namely, No.11, No.21, No.23, were ball-milled with each clay. After ballmilling for a period of twenty-four hours five percent solutions by weight of the mixture were made.

b. To solutions of clay were added solutions of the three Daxads used so that a five percent solution resulted.

c. To solutions of the three Daxads was added dry clay so that a five percent solution by weight was obtained.

A similar group of solutions was made up and to each combination with each clay was added varying quantities of the electrolyte NaCl in the following percentages: 0.10%, 6.5%, 1.03%, 1.65%, 2.32%, 3.45%, 4.53%, and 5.39%.

All of these solutions were made up with the aid of a high speed stirrer.

These solutions were made up at such times so that they were allowed to stand two weeks before their yield value was determined. All possible combinations of Aqua Gel with Daxads and salts were made for a second time, the yield value being determined the day on which the solution was made up, after having been agitated on a horizontal shaker for four hours.
This comparison was made in order to try to arrive at some conclusion as to the manner in which time and the environment might affect the results.

The yield value of the clay suspensions which may be defined as that amount of work or force which must be exerted on a solution before it will begin to flow was determined by the use of a Stormer viscometer. This instrument because of its ruggedness and comparative ease in cleaning is a very popular device for measuring viscosity in the field. It consists of a cylinder or spindle which is rotated in the test cup (in which is placed the solution) by a pair of gears which are driven by a falling weight. The rotation of the cylinder is indicated on a revolution counter. In order to calibrate the machine against water, water was placed in the test cup until the inner vanes were completely submerged. The cup was then placed in the water bath and the entire assembly then pushed upward as far as it would go on the support rod and it was held in place by a set screw. The spindle was then allowed to rotate by releasing the brake screw on the gear case. Various weights were then added to the plumb line and the
number of seconds (to tenths of a second) that it took the cylinder to make seventy-five revolutions was recorded, for each weight, after the reading had become constant. The driving weight in grams was then plotted on the "x" axis versus the rate of shear or \( \frac{1}{\text{Time}} \) on the "y" axis, the points when connected forming a straight line. This straight line, however, cut at some point above the origin indicating that there was friction in the machine. In order to correct this, a straight line, with the same slope, was drawn parallel to the first line which had been obtained. All calculations made throughout the rest of the experiment were made on the basis of this correction. The same procedure was then followed to secure the yield point of the muds, the apparent point at which the line cut the "x" axis being designated as the yield point or yield value.

In all cases the temperature was maintained at 25°C.

In order to determine the relative plastering or wall-building properties of these muds, a constant amount of each mud was placed in a Buchner funnel and by suction the amount of time necessary for five cubic
centimeters of the solution to be removed was recorded. A manometer was used to determine whether or not there was much variation in pressure. It remained constant within one or two mm at all times.
RESULTS AND THEIR DISCUSSION

Because of the fact that impure material was used throughout this thesis in an effort to simulate material which is used in the field, from a purely scientific point of view it would prove unwise to draw any definite conclusions on results which might be obtained from this work. Although approximate analyses of the clays which were used in the work are to be had, lack of knowledge of how these constituents actually are combined in the structural lattice of the clay and of the amount of impurities associated with them makes it impossible to draw any pertinent conclusion which would most probably not hold true with pure material nor with other impure material which might vary from it. Therefore, the author proposes to present the results of the experimental work with these thoughts in mind, presenting hypotheses when the situation appears to merit such.

The addition of the Daxads to Aqua Gel in all its various combinations proved effective in dispersing the Aqua Gel to some degree. The procedure of drymilling the clay and the dispersing agent together seemed to
prove to be the most effective. This is most probably due to the fact that by this procedure the individual particles of both materials were disseminated more thoroughly. When placed in contact with water the Daxad was able to prevent the formation of many agglomerates, the added repulsive forces throughout the system being more effective. (Causing it to become more fluid). See Fig.2,3,4,5. The combination of dry clay to the Daxad solutions proved to be of intermediate effectiveness between the procedure of drymilling and that of adding Daxad solution to the clay dispersion. This evidently was because it was easier for the solution of the Daxad to wet the dry clay more effectively and thereby exert its forces over a larger area than it could in the dispersion of clay. In the latter case the solution of the Daxad was in contact with a part of the clay dispersion for a longer time and "spent" more of its power of dispersion on that one part than it did on the other after it became thoroughly mixed. (see Fig.5)

After the addition of various percentages of salt to the clay-Daxad dispersions, it proved to be very difficult to determine the yield point of the
solutions. This was believed to be caused by the solutions building up a structure and displaying the property of thixotropy during intervals when weights were being changed and when small weights were in use. The latter cause was particularly marked as can be evidenced from the number of readings in the progress sheets which had to be taken before a constant value was obtained. However, the extrapolation of the yield point was at times difficult (see Fig. 6-15), for when the points for the driving force in grams versus \( \frac{1}{\text{Time}} \) were plotted, rather than giving a straight line as had water, a curved line resulted. The slope of the curved line appeared to change rather suddenly near the point where the smaller weights were used. The yield point was obtained by connecting with straight lines those points which could be so connected, the point where the line connecting the smallest weight used intersected the "x" axis being designated as the yield point.

It was found that upon the addition of different quantities of electrolytes to the clay dispersions with and without Daxads, if the extrapolated yield points were plotted versus salt concentrations
that curves as are shown in Fig. 16, 17, and 18 resulted.

In order to explain these curves intelligently, it must be kept in mind that Aqua Gel is a sodium clay and that comparatively no more negative charges can be taken on to the inner layer. It must also be assumed that the Aqua Gel contains many sodium ions for counter ions as is demonstrated by their enormous swelling in water.

On the basis of the Donnan Equilibrium (see Appendix for explanation in detail) if there are no free ions in the dispersion medium (an ideal case never realized) we may say that the osmotic pressure is at a maximum and that it is directly proportional to the number or concentration of the ions within the micelle. However, if an electrolyte is added to the solution, the electrolyte ions tend to penetrate into the diffuse double layer. A distribution of ions results in such a fashion that the ratio of the number of particles within the micelle to those outside of it has decreased. It follows from this that the excess osmotic pressure which is dependent on the concentration of the ions within the micelle will decrease as will the swelling.
With this decrease in swelling and decrease in repulsive forces, the particles are allowed to come somewhat closer together and therefore more mechanical energy is necessary to produce shear when force is applied. Hence, a higher yield point will be observed. As we add more electrolyte, the Na ions in the diffuse double layer continue to be crowded in and they tend to discharge the particle. Larger amounts of water are released from the particle as more ions go into the micelle and the particles come closer together, their kinetic energy bringing them together, and coagulation results. This release of water makes the system more fluid and the yield point as a result is decreased. (Refer to Fig.16,17,18) As larger quantities of NaCl are added the particles are discharged much more rapidly and in doing so entrap water in large amounts within the agglomerates or "hydroflocs" and again more mechanical energy is necessary to produce shear, an "apparent structure" prevailing because of these dense aggregates. If still larger quantities of NaCl are added, the NaCl is able to act more effectively and penetrate into the larger agglomerates which may form and tend to coagulate the material so that smaller flocs result which tend to make the system more
fluid.

Visual evidence for these phenomena was observed through a study of these solutions with a dark field microscope using a Cardioid Condenser. The solutions to which had been added smaller amounts of electrolyte contained particles which were relatively far apart, the distance between them decreasing progressively until the points on the first maximum of the curves in Fig.16,17, and 18 were reached. In the vicinity of the maximum the particles did not display much activity or mobility. In solutions around the region of the first minimum, some evidences of coagulation were noticeable and in addition a few of the particles were still in motion which in both cases seems to prove the point of a decrease in yield value. In regions around the second maximum, very little movement was observed and the particles could be seen massed together in huge agglomerates with rather dense mucous-like material between them. Further study of solutions in regions beyond this second maximum showed much smaller agglomerates to be present and some of the particles displayed Brownian Motion. This picture again fitted the fact that the yield point has decreased in that vicinity.
The mechanism resulting in these curves may also be explained by a slightly different theory which resembles somewhat to the Hauser Hirshon theory. Upon the addition of rather small quantities of electrolytes, (remembering that the Aqua Gel particles are nearly completely saturated) a decrease in the relative number of ions present within the micelle will occur. As the water is pushed out by the incoming ions the yield point is increased as the particles come closer together. It may be assumed that as more Na ions are able to crowd into the micelle (which may be tending to coagulate the particles) that an excess negative charge exists in the dispersion medium which may repulse the particles and prevent them from coming too close together. As a result, the system is more fluid and this fluidity may be seen in Fig.16,17,18. Upon the addition of more electrolyte the system would be coagulated and agglomerated and tend to produce a dense structure which would require added mechanical force to disrupt it. Upon the addition of more electrolyte the system may be effectively coagulated into smaller agglomerates which would require less force to produce shear and hence result into a more fluid solution.
In the short study of the wall plastering power of these solutions it was found that the solutions retained as a rule more water in regions of high initial viscosity than they did in regions of low viscosity (see table in Appendix). Further addition of salts appears to disrupt their wall-building properties. Similar results have been reported to the American Petroleum Institute according to P. Evans and A. Reid. It must be kept in mind, however, that not all systems of high viscosity will give good plastering power, because if the viscosity is due to large agglomerates water may be able to find its way through the particles rather readily.

In studying the dispersibility of the following clays: Boganite, Spudmud, Tennessee No. 1 SGP, Tennessee No. 7, Black Monroe Wad, K. T. Ivory, and Grundite it was found that the results varied so much that no definite conclusions could be drawn. The relative lowering of the yield points of various combinations of Daxad on the various clays may be seen in the histograms fig. 19, 20. Analyses of these clays are also found in the appendix. The apparent increase in yield point in certain instances must undoubtedly be due to the formation of
systems which were less mobile than they were before the addition of the "dispersing" agent. This may have been brought about by the exchange of some of the substances present in the clay by the $\lambda$xads. Electrolytes were added to these clays but they flocculated immediately so the yield point values for these solutions were not determined.
CONCLUSIONS AND RECOMMENDATIONS

1. By figures 16, 17, and 18 it has been demonstrated that Daxads may be successfully used as dispersing agents in drilling muds. In all cases except with a solution of Daxad 11 and a solution of Aqua Gel the viscosity of the treated mud was lower than that of the untreated, in the lower concentrations of salt. In ranges of higher concentration of salt the viscosities of the treated solutions were slightly higher.

2. In order to explain the phenomena which occur when salts are added to Aqua Gel in present day knowledge we must assume that the Aqua Gel under study was already saturated to a great degree with counter ions.

3. Results of this work point to the fact that no definite progress will be made in this field of research unless a pure product is used at the start in order that a perfect understanding of exactly what changes are taking place in the system maybe had.

4. Further work should be done along the lines of the
relationship of the agitation to which mud is subjected and the viscosity of the mud. The relationship of the age of the mud and its viscosity should also be studied. It was found in this work that the viscosity increased with age, but that the same general type of curve resulted when the yield point was plotted versus salt concentration.

5. A modification should be added to the Stormer Viscometer in the form of a means of keeping the liquid in the test cup in motion at all times, so that discrepancies in the actual yield point will not arise.
ROTARY-TYPE DRILLING RIG
DEFINITION OF BENTONITE

It has been proposed by Ross and Shannon \(^\text{11}\) that the name "bentonite" should include all of those rocks which contain at least 75% of the crystalline clay-like minerals montmorillonite or beidellite which are formed by the alteration of igneous materials. It has been suggested that if the clay-like material contains between 25-75% sandy material that it should be called an arkosic bentonite and that if it contains less than 25% bentonite that it should be called a "bentonitic arkose". This terminology has resulted in general confusion and it has brought about the designation as bentonite many materials which differ to a large extent from that material which was found originally in the Benton formation in Wyoming. The present trend today is to designate to those materials which are composed of at least 75% of the swelling type montmorillonite the term "bentonite". To those clays which on contact with water show no appreciable swelling should be applied the term "sub-bentonite" or better still "metabentonites" which indicates that metamorphism has taken place to alter the physical properties of the minerals where the chemical properties and origin have been common ones.
STRUCTURE OF BENTONITE

Aqua Gel may be considered as a sodium montmorillonite. Montmorillonites are a very important member of one of the groups of clays of the same name. Montmorillonite particles are composed of two silica sheets and a gibbsite layer "sandwiched" in between, joined to each other by shared oxygen atoms. By a silica sheet is meant an aggregation of silicon oxygen tetrahedra joined so that the oxygens are shared and a hexagonal net work results. A similar sheet may be made by joining aluminum octahedra together and saturating all remaining unstaturations with hydrogen. This is called a gibbsite sheet. By condensing a gibbsite sheet and two hydrated silica sheets, montmorillonite is formed.

Montmorillonites owe their remarkable swelling properties to cations which may be adsorbed at different points on their lattice. Whenever the lattice planes are broken on the sides of one of the plate-like particles, a cation may be held by the free valence of the oxygen ion. Thus in Fig. A, the lattice is broken on both the right and the left and there are many oxygen ions with unsatisfied valences. A second type exchangeable cation arises from the
possibility of a replacement of hydrogen by a cation from one of the OH groups which are attached to the aluminum. The size of the cation to be adsorbed would be of much importance here, however, because it must be of a type small enough to penetrate between the silica-oxygen planes before it can exchange the hydrogen. A third type replacement may be the one which might accompany the isomorphous replacement of silica by aluminum in the silica layer or the replacement of aluminum by magnesium in the aluminum layer. Adsorbing a cation is necessary in this case to compensate for the negative charge resulting. A fourth probable type of replacement may take place if a water molecule reacts with an oxygen ion at any point on the surface of the lattice to form two hydroxyl groups. These hydroxyl groups might in turn have removed from them the hydrogen by another cation.

"The relative quantity of the various types may vary with the origin of each particular type of bentonite." It is this variation which produces different reactions among several bentonites and which makes it difficult to foresee exactly how the material will behave.
**THE DONNAN DISTRIBUTION OF IONS BETWEEN THE MICELLAR AND THE OUTSIDE SOLUTIONS**

- **Micellar Solution** $V_1$
  - Micellar ions = 12 (all in $V_1$) conc. = $z$
  - Free cations = 12
    - 4 in $V_1$ conc. = $y$
    - 8 in $V_0$ conc. = $x$
  - Free Anions = 12
    - 4 in $V_1$ conc. = $y$
    - 8 in $V_0$ conc. = $x$

- **Outside Solution** $V_0$
  - $x^2 = y(y + z)$
  - $8^2 = 4(4 + 12)$
  - $64 = 64$
  - $2y + z - 2x = e$
  - $e = 20 - 16 = 4$

$V_1 = V_0$
In Fig B, two spheres representing a Na-saturated and a Ca-saturated micelle are shown. The micelle consists of the colloidal particle or ion complex; the atmosphere of dissociated, diffusible ions; and the osmotically imbibed water.

The great imbibition of water by the Na-saturated colloid as compared to the Ca saturated material can be ascribed to a greater dissociation of the Na ions. This causes a greater osmotic pressure around the particles which are therefore pushed farther apart by the greater osmotic inflow of water.

The swelling of a colloid saturated with nay cation will be at a maximum in the absence of free electrolytes. In order to show how a free electrolyte may suppress the swelling, let us refer to Fig.B, using as a specific case to simplify matters, a univalent salt.

$V_1$ represents a small volume within the micellar solution of a Na saturated colloid and $V_0$ represents an equal volume in the outside solution. Assume therefore that the concentration "z" of the micellar ions, i.e., ions dissociated by the particles, is such that there is an average of 12 ions in $V_1$. If there were no free ions in the dispersion medium (an ideal case
never realized) then the osmotic pressure would be directly proportional to "z" and it would be at a maximum.

If we now let the total outside solution be equal to the total micellar solution so that $V_1$ and $V_o$ represent the same fraction of each and suppose we add so much of a univalent salt, e.g. NaCl, to the system if this were equally distributed there would be 6 cations and 6 anions in both $V_o$ and $V_1$, or together 12 ions of each kind on both sides.

According to the principle of a constant ion product the distribution of these ions must follow the Donnan equilibrium equation which in this case demands that the product of the ions in $V_o$ must equal the product of those in $V_1$. Thus,

$$x^2 = y(y + z)$$

where $x$ is the concentration of each of the ions of the salt in $V_o$ and $y$ is the concentration of these ions in $V_1$ whereas $z$ is the concentration of the Na ions dissociated by the complex.

To satisfy the equation the figure shows that at equilibrium there would be 4 cations and 4 anions
of the added salt in $V_1$ and 8 of each of these in $V_0$.

By summing up all of these ions in $V_1$ and all of those in $V_0$ we find an excess $e = 4$ ions in $V_1$ whereas in the absence of any free electrolyte the excess in $V_1$ was 12. The greater we make $x$ and $y$ the smaller will be "$e"$ as compared to "$z"$, and since the excess osmotic pressure in $V_1$ is proportional to "$e"$ it follows that the osmotic swelling of the colloid will be suppressed by the addition of a salt and that the greater the concentration of the salt the greater will be this suppression.

ORIGIN

The formation of bentonite as a product of the geologic alteration of volcanic glass or ash has been postulated by Wherry, Nelson, and Ross and Shannon. The evidence for this includes the existence of thin sections of bentonites which have the same structure as the volcanic ash associated with it; the presence of feldspar and the absence of appreciable amounts of quartz (which is usually found in ordinary clays); the chemical composition of the bentonite itself which would be expected to result from the partial alteration and leaching of volcanic material by water; the field relations such as the presence of alkaline salts nearby (which probably resulted from the decomposition) and the extension of the individual beds, often very thin and of uniform thickness, over very large distances (which would most probably result from the settling of ash from a volcanic eruption). In addition to these evidences, an evidence of an experimental nature exists. In the laboratories at Massachusetts Institute of Technology a research problem was carried out in which powdered glass was placed in a crucible with several reagents such as
water, sulphuric acid, sodium, potassium, calcium, and magnesium hydroxides. The crucible and its contents were maintained at a specified pressure and were thermostatically controlled. The resulting products were non-swelling "bentonites", formed in both acid and basic solutions which compares to the metamorphosis of such in nature. These noncolloidal montmorillonites are perhaps another stage in the formation of clays, because the experiment showed that montmorillonites were merely an intermediate step. This fact was established when montmorillonite once formed was subjected to further heat yielded an entirely new product. The reason that montmorillonites are apparently not undergoing any change today is that conditions necessary to effect such a change are no longer present.

Wherry points out that these deposits have been formed during explosion from a volcano, the distribution having occurred by air currents in contact with corrosive gases which attacked the surfaces of the particles and rendered them open to rather rapid disintegration when the ash fell in moist climates.
or in shallow bodies of water. The transportation of ash in this manner can be very well visualized when one takes into account the well known fact that ash has been known to circle the earth during the largest volcanic eruptions as has been revealed by the sediments. These conditions were believed to have existed about one hundred to one hundred twenty-five million years ago during Cretaceous time. On being deposited the partly changed ash was acted upon by waters, which caused the ash to disintegrate into hydrous silica and alumina with colloid particles and bases to dissolve. Part of the soluble salts of the water are believed to have been adsorbed and the rest leached out. It is believed that this state was followed by the incipient growth of crystals from many nuclei - the entire mass being made up of minute crystal grains in contact with one another - the crystal leaves being capable of separation into flakes of colloidal thickness.

By the process of alteration the volcanic ash or glass was gradually altered to the gelling, paste-forming bentonite of today. After the bentonite had been formed two things continued to increase its stiffness. The physico chemical action of alkalies or
salts from soluble formations may be leached into the bentonite and in contact with water continue to bring about the electrolytic effect and the consistency of the bentonite was kept either in equilibrium or increased. The fact that bentonites possess the property of thixotropy which is the physical property of setting to a jelly-like consistency when allowed to come to rest and reverting to a liquid when agitated may have aided in its maintenance.²²

Although most bentonites are believed to have been formed from volcanic ash, it has been pointed out by Ross and Shannon that some deposits have been formed by the devitrification of not only glassy igneous ash or tuff but occasionally of lava flows and even of hypabyssal intrusives. Kirkman of Idaho substantiates his belief that bentonites found in Idaho are formed through the alteration of acid lavas not necessarily of a glassy texture by submitting specimens one of which contained fresh lava and bentonite and others which showed slightly altered acid lava in part to bentonite.²³
Another unusual occurrence of bentonite has been found near Daggett, California by Melhase who states that bentonites in this vicinity have been found in "pockets" or irregular masses of ten to two hundred tons, in rhyolites, being separated from one another by distances of several hundreds of feet. These rhyolites are of Tertiary age. The bentonite exhibits no evidences of stratification or transportation and appears to be clearly the result of the alteration of the rocks in situ.
FIELD OCCURRENCE

The bentonite outcrops are both unusual and striking. Due to the peculiar physical properties of bentonites, the wetted surfaces reveal a coral-like appearance having been formed by the alternate swelling and shrinking of different parts of the substance due to the repeated wetting and drying, which is a reflection of variation in composition. After a rain, many bentonite outcrops are covered with a thick mass of slippery jelly but in dry weather this same surface may be found to have a dry, fluffy, or peculiar granular appearance. Others are found to possess a greasy appearance and feeling. Slight conchoidal fracture may at times be perceived whereas in other cases the bentonite may exhibit shaly cleavage.

Nearly all bentonites contain gritty or sandy inclusions and these may be removed before marketing for they are considered as impurities. Pulverized bentonite is usually fine grained and light colored, ranging from cream to olive green; but it has also been found to be pink, dark brown, or even black. However, after firing, the color is usually white, buff, or light brown.
The coloring of bentonites offers a very interesting problem which has not as yet been solved. Some people attribute its color to the impurities which it contains. Others are of the opinion that the colloidal size of the particles bring about these variations. No other state of matter exhibits more varied or more strikingly beautiful colors than does the colloidal state. It is believed that the color phenomenon is due to the unique relationship between the wave length of white light and colloids.
DEPOSITS - MINING AND PRODUCTION

Wyoming

The stratified bentonite deposits of Wyoming which range from a few inches to as much as twelve feet in thickness are usually a soft, green, wax-like material with a high luster. On drying the color becomes lighter and the luster duller. Gypsum crystals as long as three inches are often found weathered out on the outcrops. It has been found by observation that the outcrops vary largely in color and in luster and in composition in the different parts of the state. It was at first postulated that these variations were due to the degree of folding or metamorphism to which the beds had been subjected. However, after more detailed work had been done, it was found that beds within the same formation were often found to maintain their color when there was as much of a difference as ninety degrees in the dip. This variation in color is believed to be due to differences in the conditions of deposition, to difference in the degree of alteration after its deposition, or to a difference in the distance from the
source of supply of material from which it was derived.

The areal distribution of bentonite in Wyoming is rather widespread. Large amounts are found in the northeastern part of the state in the Black Hills Region. The formations in which it is found at this locality are the Mowry Shale and the Belle Fourche Shale which are the upper two members of the Graneros formation. The Mowry is a succession of black siliceous shales containing many fish scales and its thickness averages about one hundred fifty feet. The Belle Fourche Shale is a succession of thin, soft, dark black shales containing many siderite concretions which measure up to six feet in diameter. These concretions are locally known as "turtle backs". In the Big Horn Mts. the outcrops of bentonite are found on the east flank and on the south and east sides of the Big Horn Basin which lies to the west of the mountains. The beds in which the bentonites are found in this locality are the Thermopolis, the Mowry, and the Frontier. Bentonite seams are found on the northeast flanks of the Wind River Mts. and also in the central and southeastern parts of the state. They occur in the same formations (or
their equivalents) as in the other parts of the state. However, in the southeastern part, bentonite is also found in the Steele formation which is younger than any of the others mentioned. The structures are rather extensive in some of these parts of Wyoming and the bentonite beds are often found standing out in relief.

The overburden on some of these beds is often as thick as thirty feet and it is removed by scrapers and tractors supplemented with power shovels on beds that are deeply covered. Sometimes bentonite which contains less than thirty percent moisture will break from the ledge with a conchoidal fracture when it is struck with a pick. Sometimes the bentonite is removed with steam shovels, but it is more advantageous to load it by hand because in doing so a more pure product is assured. If the weather is quite cold, blasting may be necessary to remove the bentonite.

Some of the treatment plants are near the deposits and the producers usually transport the material in cars running on tracks. If the plant is a little distance away, trucks may be utilized.
The milling of the bentonite consists of drying with care (to avoid overheating), crushing, and grinding to specific sizes desired. The usual size of the ground material is ninety percent -200 mesh. This may be made smaller if desired. The ground bentonite is shipped in either cloth or paper bags for hygroscopic moisture causes little or no difficulty. Direct contact with water must however be avoided.

**Arizona**

Within the last ten years there has been reported by V.T. Allen some Triassic bentonite in the Painted Desert of Arizona bordering the eastern edge of the Grand Canyon National Park in Coconino County. A steady production of the bentonite has been carried on for the bleaching of oils.

**Arkansas**

Small deposits of bentonite have been found in Cuchita County which were commercially mined for a few years but which are no longer being worked at the present.
California

The largest deposits from California occur in the arid desert regions along the Amargosa River in Inyo County. The material from these deposits is known as shoshonite and amargosite and its analysis corresponds to that of montmorillonite. Its characteristics, however, are entirely different from those of the Wyoming variety. At Ash Meadows, the Standard Oil Co. mines bentonite from beds four to twelve feet thick which are overlain by 50-100 feet of sandstone, clay, or marl. Stripping of the overburden proved impractical in this case so drifting methods are now used. The main haulageways are timbered and no difficulty has been encountered in supporting the roof. The overburden in this case is very well consolidated and firm but the bentonite is so full of water that it has the tendency to heave and it has in many cases been found to heave to such a degree that it completely blocks the workings. Airtight doors are provided at the entrances so that an unnecessary drying and crumbling of the bentonite is prevented. The desiccating atmosphere out of doors removes the moisture in three or four days after
which the material may be shipped to refineries for further treatment.

Bentonite which can be used for filtering purposes is found near Shoshone and an ample supply for many years to come has been blocked off. In this locality the overburden is very thin and it can be very easily scraped off.

Otaylite, a deposit of bentonite locally known by that name, is found in San Diego County. Ladoo reports that this clay forms a lenticular bed and that it is composed of very numerous thin strata of colors ranging from white to green, pink, and chocolate, all of which have the same composition which resembles that of bentonite. For commercial purposes these are all blended together so that a product of uniform color is obtained. Although these strata are all very well drained so that no water is encountered in mining operations (which are conducted by stripping or drifting) the bentonite is always quite moist and contains about thirty percent water. However, the percentage of water may be greatly reduced by exposure to the air for several days.
Bentonite has been found to occur in masses in San Bernardino County. These deposits range from 10-200 tons. A very white waxy substance which consists mainly of hydrous magnesium silicate, with small amounts of flourine, sodium oxide, aluminum, and exceedingly small amounts of iron, has been found to also occur in this region. It possesses many of the gelling, swelling, and other characteristics of Wyoming bentonite. This product has been successfully tested in the Lance Creek Oil field for deep well drilling by the rotary method and it gave better results than any other drilling fluid previously used. In addition it has been found to be excellent in foundry work.

It is in Kern County that the bentonite was found that is believed to be derived or to have been formed as an alteration product of rhyolites. It is white in color and it is estimated that it will take up about sixty-four times its bulk of water. However, the author is of the opinion that this may be a gross error for no other known material has ever been found capable of doing this. Furthermore, it is reported that these beds are too impure to be of much value. If these beds are so impure it is difficult to under-
stand how so much water could be imbibed because the amount of water imbibed depends on the available ions in the space lattice of the mineral and if the material contains a large amount of impurities, this capacity would be lessened. It is believed that these beds are possibly of Pliocene Age. They are largely covered by lavas and lake beds.  

Colorado

A very large amount of bentonite of excellent grade is found in Lost Canyon ten miles north of Gunnison. The properties of the bentonites and metabentonites which occur in the eastern part of the state have been studied with much detail. A large deposit of pink bentonite has been found near Silver Cliff in Custer County. Bentonite with good swelling properties is reported near La Junta, Colorado.  

Idaho

The development of the few bentonite deposits which have been found in Clarke, Custer, and Mesquite Counties has been limited. Hence, very little information on their properties is available.
Mississippi

Bentonite suitable for bleaching clay has been reported in Monroe and Prentiss Counties and high quality bentonites occur in Wayne and Smith Counties. These deposits have, however, not been developed extensively.

Nevada

Very little commercial production of bentonite has been reported in Nevada during the past few years regardless of the fact that many good deposits are known to exist. In the past, large quantities of bleaching clay have been mined in Nye County. These clays are found in Tertiary beds. A deposit which closely resembles the Wyoming product has been reported in Esmeraldo County. This material occurs in bedded layers in what was formerly believed to be a lake. Nearly pure volcanic ash is found at the top, bentonite with some gangue is found immediately below and on the bottom is found a bed of quite pure bentonite. The bed in which the clay occurs is believed to extend at least five miles.
New Mexico

Very little bentonite is produced today in New Mexico although several very significant sources are known. It is perhaps due to the geographical location of the deposits that they are not being mined at present. Rather extensive deposits are found just north of Santa Fe and in Rio Siriba County. In Eddy County, oil well drilling has revealed the presence of bentonite in Permian strata.

Oklahoma

The known bentonite deposits of Oklahoma are restricted to Woodward and Dewey Counties. These should rightfully be called "sub-bentonites" because their aluminum content is mostly dissolved by the action of sulphuric acid. After activation the clays may be used for bleaching purposes. Whether or not other deposits of the so-called "bentonites" are actually such has not as yet been determined.

South Dakota

Although South Dakota has many bentonite beds which are similar to those which are found in the Black Hills of Wyoming, in comparison, very little has been
mined. The lack of production is perhaps because of inadequate milling facilities. It has been reported, however, that plans are being formulated for the construction of new mills.

**Texas**

Clays of the nonswelling or metabentonite type occur in considerable quantities in Texas and their most important uses are in drilling fluids and in bleaching oils. The majority of the producers in this state are various oil companies who consider it more profitable to mine their own material.

**Utah**

The major production comes from Aurora and Sevier Counties.

**Washington**

Important deposits of high-swelling bentonite of the montmorillonite type is found in the vicinity of Seattle.
Canada

In spite of the efforts of the Mines Branch of the Canadian Dep't. of Mines to stimulate production of bentonite in Canada from its domestic sources little production has as yet taken place. It is believed that bentonite is widely distributed over southern Alberta and Saskatchewan but that due to the level terrain and paucity of deeply cut drainage channels good outcrops of Cretaceous rocks are rare. Therefore, it is only in the region of the badland topography as in the valley of the Red Deer River or where the Cretaceous beds occur as knolls or along coulées that bentonite beds are available. However, the sticky nature of the prairie gumbos and the sloughs indicates that it is probably due to the presence of bentonite or bentonitic sandstones and shales. This would lead to the conclusion that there is a widespread occurrence of bentonite in the Prairie Provinces.37

Italy

The Isle of Ponza in the Pontine Island of Italy is said to possess one of the largest known oc-
currences outside of the United States. Although its swelling and gelling properties are inferior (it is a calcium bentonite—the Ca counter ions being less capable of hydration is not able to promote as much swelling as is the Na ion) due to the fact that the bentonite contains a very low percentage of iron it is considered extremely useful in the ceramic industry.

Other Countries

The many industrial applications of bentonite have stimulated the search for commercial deposits throughout the world with the results that occurrences have been discovered in Russia, Poland, Germany, Rumania, France, South Africa, China, Japan, New Zealand, and Mexico. However, these deposits have not as yet developed to a great extent.

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Legend to Map

1. Coconino County, Arizona
2. Ouachita and Dallas Counties, Arkansas
3. Inyo Co., California
4. San Diego County, California
5. San Bernardino County, California
6. Kern County, California
7. Gunnison County, Lost Canyon, Colorado
8. Custer County, Colorado
9. Owyhee County and Cassia County, Idaho
10. Custer and Clark Counties, Idaho
11. Monroe and Prentiss Co., Mississippi
12. Wayne and Smith Counties, Mississippi
13. Nye County, Nevada
14. Esmeralda Co., Nevada
15. Dona Ana Co., New Mexico
16. Santa Fe County, New Mexico
17. Eddy County, New Mexico
18. Sierra County, New Mexico
19. Woodward County, Oklahoma
20. Butte County, South Dakota
21. Colorado County, Texas
22. Sevier County, Utah
23. Medicine Bow, Carbon County, Wyoming
24. Johnson Co., Wyoming
26. Seattle District, Washington
27. La Junta, Colorado

It is of geological interest to note that the majority of the bentonites found in Wyoming, Idaho, South Dakota, and Washington are Aluminum bentonites. Most of the bentonites found in California, Nevada, Utah, and parts of Colorado and perhaps northern New Mexico are Magnesium bentonites, whereas those bentonites which are found in southern New Mexico, Texas, and Oklahoma are unsubstituted bentonites.

The variation in the composition of the bentonites may be postulated to be due to their having been laid down in shallow seas which possessed different sources and hence contained different minerals; or that after these bentonites were deposited, that encroaching seas from different directions or even ground water from different sources so altered them.
PRESENT AND PROPOSED USES

Prospectors who become interested in the production of bentonite should make a careful investigation of the commercial possibilities of any deposit before investing too heavily in it. They should study the possibility of marketing the product; the specifications demanded; the price which may be obtained for it; the cost of mining, testing, treating, and shipping; the size of the deposit, and the nature of the crude bentonite. The consumers of bentonite desire a homogeneous product and deposits which are homogeneous on the outcrop and which will continue to possess this property after continuous mining are not very common.

**Filler, Binder, Plastic**

A filler is a finely divided inert substance which is added to give "body" or weight or to produce some other desirable physical condition in another substance. It may be mixed with other ingredients to form an integral part of a body or it may be applied in the form of a wash or a suspension to fill pores or to form a coating. The general charac-
teristics which are desired for such work are: an extreme state of fine division; the property of remaining in suspension; plasticity; and high absorbent power. All of the properties are possessed by purified, ground, alkali bentonite.

a. Paper, oil cloth, curtain cloth, linoleum, and cordage.

The paper manufacturer uses most of the clay which is used in the filler industry today. Properties which are desired are: the absence of grit, a white color, and retention. These requirements rule out a large percentage of the bentonites because light colored ones are rather rare. Alkali bentonites give a superior feel to paper and overcome the gumming of the screens used in the pulp industry by forming an emulsion with the resin which ordinarily gives all of the trouble. However, most bentonites are rejected in most of these industries because of their cost.39

However, not only is the bentonite used as a filler in paper, but through recent research work at Massachusetts Institute of Technology, Cambridge, Massachusetts, it has been possible to form a very high grade of paper merely by dispersing concentrated mono-
disperse particles of bentonite, spreading them on a flat surface, and allowing them to dry. The individual particles by the concentration have had their Brownian Motion decreased so that an equilibrium condition is present in which the particles are spaced apart at very small distances due to the repulsive forces which they possess. When the evaporation is begun, the individual particles which are absolutely stationary are suddenly mechanically driven together and as they reach a certain distance they snap together in an oriented position. If nothing was added to the clay sol before evaporation, the resulting sheet of paper naturally exhibited swelling properties when placed in contact with water. The fact, however, that hydrogen bentonite, when once completely dehydrated can no longer be dispersed in water is easily shown with these hydrogen bentonite films. Films made from this type are very fragile. During the research on this problem it was kept in mind that natural Na bentonites have a very high base exchange capacity so the "Alsifilm" (name applied to this "paper") was immersed for different lengths of time in saturated solutions of KOH (saturated so that no peptization might take place - so that complete discharge of the
particles might occur at once) and it was found that complete replacement of the Na had taken place. These sheets on being immersed in water for several days were found to have picked up only a very small amount of water and they no longer showed any property of swelling. Similar results were obtained when the Na clay was base-exchanged with a lead acetate solution. Other ions such as Ag were found to base exchange completely, also, but they were not found to be resistant to water. This may be explained by the fact that the Ag ions are smaller and they could not serve to bind the particles together as could the K and Pb. The structure of these films when studied with X-Ray show that the individual lattice layers lie parallel to each other at a slight angle, their "C" axis being perpendicular or at a slight angle to the plane of the film. This apparent structure may be shown by striking a film of hydrogen bentonite in one spot and the film will tend to bend on both free ends. If the film is then turned on the other side and hit in the same spot, the sheet will first unfold and then turn up again on the two free ends. This phenomenon will not occur, however, if electrolyte-treated films are used. Besides being absolutely water resistant, it is
resistant to hot water, to acids for a long period of time, to electrolytes, to grease or oil, to organic solvents, and to high temperatures. Alsifilm possesses good dielectric properties which is not very strange due to the fact that it has been made to resemble mica as closely as possible. The material may be softened so that it is flexible; may be made crease proof. The fact that Alsifilm possesses guaranteed uniform thickness and texture makes it supercede mica in some respects. All sorts of ingredients such as dyes and pigments may be introduced into it. By adding titanium it is possible to secure paper which has an exceedingly high gloss and which may prove to be valuable in preserving important documents. The disadvantage which paper of this sort displayed in its early stages of experimentation was poor tear resistance. However, this disadvantage has been remedied by incorporating into it fibers which will increase the tear resistance by forming within the structure of the clays an interwoven mesh which will take up the stresses as they are applied.

Although there are no definite standard tests to be used to evaluate clay fibers for oilcloth,
linoleum, curtain cloth, or cordage, properties necessary are usually freedom from grit, quick slaking to a smooth, soapy feeling cream or slip which possesses no lumps, rather low oil absorption, and in some instances pure whiteness. Regardless of the fact that bentonites have not replaced clay in these industries to a very large extent, their physical properties indicate that they could be of value for this.

b. Rubber

Bentonite is used to disperse rubber in the form of a filler. Artificial rubber can not be very easily dispersed in water because it is hydrophobic and hence resists water. In order to be able to disperse it, bentonites and water are added to plastic rubber and the milling is continued. The swelling of the bentonite exerts a pressure and tends to reduce the walls separating the bentonite from the rubber. Finally, after the addition of more water, the wall so-formed is broken. The rubber particles at this stage are surrounded by bentonite. Because of the apparent hydrophilic nature of bentonite brought about by the adsorbed ions on the outer later of the bentonite lattice the rubber may then be dispersed.
c. Ceramics

Bentonites have been suggested for use in the field of ceramics because of their high plastering powers. It has been suggested that they be especially used in making graphite crucibles to insure closer bonding of the graphite particles and the other constituents.

d. Portland Cement

It has been found that the mechanical strength and the time of setting may be visibly increased by the addition of only one percent bentonite, to Portland cement slurries. This quick setting must be due to the adsorption of water by the bentonite.

e. Road Building

Because of the binding qualities and its resistance to passage of water, bentonites should be of some value in the surfacing of highways. Such application has been tried on highways in Nevada. A sandy road covered with oil was overlain with bentonite. After a year and a half the road was still in very good condition. Whether or not such surfacing could be employed throughout the country is speculation because of the cost of the bentonite.
f. Lubricating Grease

Although very little work has been done on the application to bentonite to this field it is believed that it could find some use.

g. Putty

All types of bentonites are workable as putty and an appreciable decrease in linseed oil is necessary for its making. One disadvantage which might influence its use in this field is its color.

h. Foundry work

Bentonite may be used as a bonding agent in the molding of sands. It is believed by some people to possess the disadvantage of dehydrating too rapidly to be of much use but other operators have found it to their advantage to use it. These operators maintain that less clay is needed to bind the sand therefore there is more space present between the sand grains to allow a more rapid egress of steam and gases created in the pouring of the metal. Bentonite also allows the sand to be worked with a smaller percentage of water which results in smaller amounts of steam being formed.
I. Phonograph Records and Electrical Insulation

The qualities which must be possessed by bentonites in order to be used for phonograph records are: freedom from grit, low adsorption for the binder used, and the bentonite particles must be able to pass through 200 mesh screens. The color in this case is of no importance. Bentonite is used in electrical equipment as an insulator because of its dielectric properties. 43

J. Pencil leads, crayons, and pastel colors

Manufacturers of pencils, crayons, and pastel colors find bentonite to be of much value to their industry because its presence increases the blending properties of the material. 43

K. Paste, glue, and sizing

As a paste or a glue, bentonite is employed because of its adhesive powers. It is used as sizing because it imparts no harm to the finished goods. Because of its inertness - a quality which is not inherent in starch - molds are not able to develop in goods in which it has been used as sizing. 43
Adsorbent, Emulsifier, and Peptizer

a. Soaps and detergents

It has been found by research that bentonite may replace as much as 25-50% of the soap substances and at the same time increase the lathering and detergent properties of a substance. This question is however definitely not settled for later work has shown that more soap is actually needed when bentonites are used because of the adsorption which it has for the soap. However, the lather which it produces is much more stable and it can therefore adsorb more bentonite which has clinging to it dirt particles which were removed by the emulsion. Bentonites in soaps give to them a velvety feel. The addition of bentonite to hard water before the soap is added will greatly decrease the amount of soap which will be used due to the base exchanging properties of the bentonite.

It is especially good in the scouring of textiles; in the production of more brilliant colors in dyed goods; in increasing the clarity and sharpness of printed materials; and in producing a "bottoming" effect in yarns.

b. De-Inking Printed Papers

Alkali bentonites have proved successful
and economical in actual practice on an industrial scale for the de-inking of old newspapers. This not only provides an outlet for bentonite but it also serves as an aid for forest conservation. This process may be accomplished by heating newspapers in a solution of caustic soda so that the carbon will have a positive charge. The bentonite has a negative charge and it is able to peptize the carbon and these together are then washed from the paper with water. The reason that this process is not utilized more is that the sources of newspapers (large cities) are far away from deposits of bentonite.

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c. Refining of fats and oils

The properties of absorption, adsorption, filtration, and perhaps chemical action makes bentonite valuable in the refinery of fats and oils. The bentonite, if the proper kind, will remove the carbon, tarry complexes, and the dissolved coloring matter. The same kind of bentonite may not be used in the treatment of all oils but laboratory tests must be run to endeavor to find the bentonite which is best suited for each particular oil. It has been found that sub-bentonites are admirable suited for this work, those having been treated being much better. 43.
The most direct use for bentonites in this field is in the decolorizing of vegetable and animal fats and oils. It is extensively used in clarifying brown packing house lard. The lard is heated and percolated through bentonite from which it emerges snowy white. After the bentonites have been completely filled with impurities so that they can no longer be used as clarifiers, they are used in the making of soap.

d. Horticultural sprays, animal dips, and insecticides

Properties which should be possessed by all sprays and dyes are: possess agents which will form permanent emulsions; increase adhesion; improve the covering effect; and promote the formation of a continuous coat. The bentonite is used as an emulsifying agent so that the oils will come into contact immediately with the surface of the leaves and will not have to wait until the water is evaporated in order to commence its work. The same principle is employed in animal dips.

e. Paints, enamels, inks

Bentonites have the power of adsorbing dyes and colors because of its increased surface area.
This plus its fine state of subdivision enables it to form stable suspensions so that it can be used in the manufacture of cold water paints, printers inks, and oil paints. It adsorbs and peptizes lamp-black and it promotes the emulsion of water in oil to form ready mixed paints so that they will not settle out.

f. Wood dips

Bentonites form emulsions of oil and water with oil as the external phase so that it may come into contact with the wood and thereby repel the water - in this manner serving to protect the wood. 43

g. Roofing preparations and water proofing

Bentonites have been used in preparing emulsions of asphalt and coal tar as roofing materials. Products of asphaltic bentonite and rosin bentonite mixtures when mixed with water make a very excellent water proof paper board. 43

h. Coal mine dusting

Bentonite ground up in fine particles is used as a spray in mines. It serves to adsorb the
charge which is propagated by small pieces of coal suspended in the atmosphere. The accumulation of these charges often result in "dust explosions". These explosions are due to the so-called "Fall Potential".

i. Desiccating agent

Bentonite has been suggested to replace calcium chloride as a desiccating agent because of the former's power of adsorption but it has not been successful to any extent.

j. Manufacture of dynamite

Because bentonites adsorb twice as much nitroglycerine as do diatomaceous earths it has been suggested that they could be used in the manufacture of dynamite. However, it has not been used in this industry because of the gritty particles which it often contains. These particles in touching each other might generate sparks.

Bentonite as a Chemical Reagent

a. Water Softener

Bentonites are used in this work because of their large base exchange capacity. The counter ions of the bentonite are able to be replaced by the less
hydratable ions which are found in the water which give to it the property of hardness.

b. Aid in soil fertility

Bentonites act as colloid material to retain the salts needed by the plants who may by selective adsorption remove those which they desire.

c. Treatment of Molasses

In the treatment of molasses a calcium zeolite has been used to remove the potassium from the molasses solution. This is done in order to insure a higher recovery of the sugar content. It is believed that a Na bentonite which had been replaced by Ca might give the same effect.

Bentonite as a Medicament and Cosmetic

a. Alkali bentonites mixed with various liquids produce plastic homogeneous bodies which possess both cleaning and healing powers. The power of the bentonite to perform this function is explained chiefly on the basis of its colloidal properties to adsorb moisture, salts, and other impurities from the surface of the body.

b. Bentonite may be used in cosmetics as a beauty clay and massage cream due to its cleansing power.
# CHEMICAL ANALYSES

## Average Chemical Analysis of AquaGel Clay (Wyoming Bentonite)

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture at 105° C</td>
<td>8.00%</td>
</tr>
<tr>
<td>Silica (SiO₂)</td>
<td>59.17%</td>
</tr>
<tr>
<td>Alumina (Al₂O₃)</td>
<td>19.08%</td>
</tr>
<tr>
<td>Ferric Oxide</td>
<td>2.79%</td>
</tr>
<tr>
<td>Ferrous Oxide</td>
<td>0.42%</td>
</tr>
<tr>
<td>Titanium Oxide</td>
<td>0.13%</td>
</tr>
<tr>
<td>Phosphoric Acid</td>
<td>0.01%</td>
</tr>
<tr>
<td>Magnesia</td>
<td>2.12%</td>
</tr>
<tr>
<td>Lime (CaO)</td>
<td>0.48%</td>
</tr>
<tr>
<td>Soda (Na₂O)</td>
<td>2.38%</td>
</tr>
<tr>
<td>Potash (K₂O)</td>
<td>0.36%</td>
</tr>
<tr>
<td>Sulphur (SO₃)</td>
<td>0.32%</td>
</tr>
<tr>
<td>Ignition Loss</td>
<td>4.74%</td>
</tr>
</tbody>
</table>

Specific Gravity varies from 2.5 to 2.7

Refractive Index 1.53

## GRAIN FINENESS BY WET MECHANICAL ANALYSIS

<table>
<thead>
<tr>
<th>Category</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Larger than 53 microns (270)</td>
<td>3.00%</td>
</tr>
<tr>
<td>Between 10 and 53 microns</td>
<td>7.00%</td>
</tr>
<tr>
<td>Between 5 and 10 microns</td>
<td>2.00%</td>
</tr>
<tr>
<td>Between 1 and f microns</td>
<td>11.00%</td>
</tr>
<tr>
<td>Between 6.5 and 1 micron</td>
<td>6.00%</td>
</tr>
<tr>
<td>Finer than 0.5 microns</td>
<td>71.00%</td>
</tr>
</tbody>
</table>

Analyses of Material used as Base for clays Boganite and Spudmud

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>70.45%</td>
</tr>
<tr>
<td>Alumina</td>
<td>12.62%</td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>3.52%</td>
</tr>
<tr>
<td>Magnesium Oxide</td>
<td>1.38%</td>
</tr>
<tr>
<td>Calcium Oxide</td>
<td>0.83%</td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>12.20%</td>
</tr>
<tr>
<td>Component</td>
<td>Tenn.1</td>
</tr>
<tr>
<td>----------------------------</td>
<td>----------</td>
</tr>
<tr>
<td>Silica</td>
<td>47.34%</td>
</tr>
<tr>
<td>Alumina</td>
<td>34.94%</td>
</tr>
<tr>
<td>Titanium Oxide</td>
<td>2.82%</td>
</tr>
<tr>
<td>Iron Oxide</td>
<td>0.599%</td>
</tr>
<tr>
<td>Calcium Oxide</td>
<td>Trace</td>
</tr>
<tr>
<td>Magnesium Oxide</td>
<td>None</td>
</tr>
<tr>
<td>Sodium Oxide</td>
<td>0.04%</td>
</tr>
<tr>
<td>Potassium Oxide</td>
<td>1.66%</td>
</tr>
<tr>
<td>Ignition Loss</td>
<td>13.13%</td>
</tr>
<tr>
<td>% Residue 120mesh</td>
<td>Trace</td>
</tr>
</tbody>
</table>
### COMPARATIVE PHYSICAL PROPERTIES OF DAXADS

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Daxad 11</th>
<th>Daxad 21</th>
<th>Daxad 23</th>
<th>Daxad 27</th>
</tr>
</thead>
<tbody>
<tr>
<td>Powder or Solution</td>
<td>Powder</td>
<td>Powder</td>
<td>Powder</td>
<td>Powder</td>
</tr>
<tr>
<td>Solubility in Water</td>
<td>Almost Comp.</td>
<td>Soluble</td>
<td>Soluble</td>
<td>May give coll.susp.</td>
</tr>
<tr>
<td>Type of Solution</td>
<td>Turbid</td>
<td>Clear</td>
<td>Clear</td>
<td>Turbid</td>
</tr>
<tr>
<td>Maximum Concentration at 70°</td>
<td>38-40%</td>
<td>25%</td>
<td>25%</td>
<td>20%</td>
</tr>
<tr>
<td>pH of 1% solution</td>
<td>7.0 - 8.5</td>
<td>7 - 8</td>
<td>7 - 8</td>
<td>7.5 - 8.5</td>
</tr>
<tr>
<td>Reduction of Surface Tension</td>
<td>Nearly none</td>
<td>Slight</td>
<td>Slight</td>
<td>Slight</td>
</tr>
<tr>
<td>Foam Tendency</td>
<td>None</td>
<td>Little</td>
<td>Little</td>
<td>Little</td>
</tr>
<tr>
<td>Wetting Capacity</td>
<td>None</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Emulsifying Agent</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Act as Protective Colloid</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Stability toward:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mild Acid</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Mild Alkali</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Stability on Boiling</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
<td>O.K.</td>
</tr>
<tr>
<td>Not Recommended for use</td>
<td>In presence of large am'ts.casein where thickening objectionable</td>
<td>In presence of soap and Ca salts</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recommended Am't. of Daxad Solid to use based on dispersed phase.</td>
<td>2-4%</td>
<td>1 - 2%</td>
<td>1 - 2%</td>
<td>1 - 3%</td>
</tr>
<tr>
<td>Sample 30cc</td>
<td>Amount Suctioned Out - 5 cc</td>
<td>Press. 722mm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------</td>
<td>-----------------------------</td>
<td>--------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% Aqua Gel</td>
<td>Time</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drymilled(Daxad 11 + Aqua Gel) +</td>
<td>6&quot; 26.2'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.32% salt</td>
<td>1&quot;10.5'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.65% salt</td>
<td>1&quot;34.2'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.03% salt</td>
<td>2&quot;19.6'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5% salt</td>
<td>2&quot;50'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9% salt</td>
<td>2&quot;7.8'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solution Daxad 11 + Sol Aqua Gel +</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.32% salt</td>
<td>2&quot;29.8'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.65% salt</td>
<td>4&quot;59.2'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.03% salt</td>
<td>6&quot;4.5'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5% salt</td>
<td>6&quot;31'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.19% salt</td>
<td>5&quot;35.5'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solution Daxad 11 + Aqua Gel +</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.32% salt</td>
<td>1&quot;39'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.65% salt</td>
<td>3&quot;57.8'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.03% salt</td>
<td>4&quot;13.8'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5% salt</td>
<td>3&quot;50.7'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.19% salt</td>
<td>3&quot;28.5'</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt</td>
<td>Sol Aqua Gel</td>
<td>Drymilled Daxad 21 + Aqua Gel</td>
<td>Solution Daxad 21 + Sol Aqua Gel</td>
<td>Solution Daxad 21 + Aqua Gel</td>
</tr>
<tr>
<td>------</td>
<td>-------------</td>
<td>--------------------------------</td>
<td>---------------------------------</td>
<td>--------------------------------</td>
</tr>
<tr>
<td>2.32%</td>
<td>2&quot;42.2'</td>
<td>2&quot;3.5'</td>
<td>2&quot;20'</td>
<td>2&quot;52.3'</td>
</tr>
<tr>
<td>1.65%</td>
<td>3&quot;8.2sec</td>
<td>1&quot;52'</td>
<td>2&quot;26'</td>
<td>2&quot;45'</td>
</tr>
<tr>
<td>1.03%</td>
<td>5&quot;2.5'</td>
<td>3&quot;12'</td>
<td>6&quot;9'</td>
<td>3&quot;40'</td>
</tr>
<tr>
<td>0.5%</td>
<td>5&quot;13.3'</td>
<td>3&quot;30.7'</td>
<td>8&quot;1.9'</td>
<td>4&quot;38.6'</td>
</tr>
<tr>
<td>0.19%</td>
<td>4&quot;37'</td>
<td>4&quot;41.2'</td>
<td>6&quot;3.5'</td>
<td>5&quot;26.5'</td>
</tr>
</tbody>
</table>
Drymilled (Aqua Gel + Daxad 23) +

2.32% salt 1"35.6'
1.65% salt 3"37.9'
1.03% salt 3"49.4'
0.5% salt 4"14.6'
0.19% salt 4"3.8'

Solution Daxas 23 + Sol Aqua Gel +

2.32% salt 4"0'
1.65% salt 4"8.5'
1.03% salt 3"48'
0.5% salt 3"42.5'
0.19% salt 3"56'

Solution Daxad 23 + Aqua Gel +

2.32% salt 2"13.5'
1.65% salt 4"20'
1.03% salt 3"43.6'
0.5% salt 5"55'
0.19% salt 5"10.4'
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TABLES
Yield Plant

Weight (Grams)

1. Sample 1
2. Sample 2
3. Sample 3
Sub (Solution) Decal 21/2 (gspat Gen) + NCC Solution

8% Decal + 92% Decal - Constant

% of NCC Variable

1 1.917
2 3.650
3 5.383
4 6.460
5 10.132
6 9.392
7 4.832

Weight (Grams)
Yield Point

- Solution Dowod 21 + Solution Aqua Gel + NaCl
- Solution Dowod 21 + Aqua Gel + NaCl
- Solution [Unmilled Dowod 21 + Aqua Gel] + NaCl
- Solution Aqua Gel + NaCl

% NaCl

0 2 4 6 8 1 2 3 4 5