

THE SYNTHESIS OF ORGANIC
DERIVATIVES OF BENTONITE

by

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INTRODUCTION

There are many different clay minerals. However, most of these may be placed in one of three main groups. These groups are kaolinite, illite and montmorillonite. Bentonite is the name applied to a clay consisting chiefly of the mineral montmorillonite, and it is to this mineral that we shall restrict our attention.

Montmorillonite has a platy structure somewhat related to the micas and pyrophyllite. Ideally this structure consists of a gibbsite layer terminated above and below by a tetrahedral silicate layer. Since the perfect or ideal seldom, if ever, is realized in nature, it is found that other elements may proxy for aluminum in the gibbsite layer and for silicon in the silicate layer. If this foreign ion bears a positive charge less than that of the element it replaces, then the lattice will become negatively charged and may attract positive ions. Other positive ions may replace these ions and it is the observance of this fact which has led to the formulation of the concept of base exchange.

Base exchange reactions are not restricted to metal ions, since hydrogen ions and certain organic cations react similarly. Probably the amines have received more attention in base exchange reactions than any other class of organic compounds, although other types of compounds are known to react with bentonite. The present work was undertaken to extend this list.

HISTORICAL REVIEW

According to Ross and Hendricks (19) it was Damour and Salvetat who proposed the name montmorillonite for a clay material from Montmorillon, France. On the basis of chemical analysis, Le Chatelier and other investigators suggested formulas for this clay.

Montmorillonite is a secondary mineral which has been formed by the chemical alteration and devitrification of volcanic ash and tuff (15). Consequently, many impurities are present in the natural clay. This fact undoubtedly led to some confusion, but isomorphous replacement and base exchange properties complicated the picture in a more subtle manner.

All these early assignments suffered most from a lack of structural information, and it was not until X-ray techniques had been developed that this information became available. Pauling (16) studied the micas, pyrophyllite, and other minerals closely related to montmorillonite. It was this basic work followed by that of Hofmann, Endell and Wilm (12) and Edelman and Favejee (6) which laid the foundation for modern views regarding the structure of montmorillonite (8).

Montmorillonite has been assigned the formula $(\text{OH})_4\text{Al}_4\text{Si}_8\text{O}_{20} \cdot n\text{H}_2\text{O}$ by Hofmann and co-workers (12), however Edelman and Favejee (6) propose $(\text{OH})_{12}\text{Al}_4\text{Si}_8\text{O}_{16} \cdot n\text{H}_2\text{O}$. It is generally agreed that the basic structure consists of two tetrahedral silicate layers with an octahedral gibbsite layer bound between them. The main

point of difference between the two structures is that Hofmann proposes an oxygen populated surface, whereas Edelman favors a hydroxyl populated surface. The following table will bring out this difference.

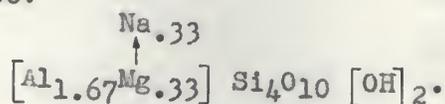
	Edelman	Hofmann	
(tetrahedral) silicate layer	$\left[\begin{array}{l} 2(\text{OH}) \\ 2\text{Si} \\ 6\text{O} \\ 2\text{Si} \end{array} \right]$	$\left[\begin{array}{l} 6\text{O} \\ 4\text{Si} \\ \cdot \\ \cdot \end{array} \right]$	
(octahedral) gibbsite layer	$\left[\begin{array}{l} 4(\text{OH})+2\text{O} \\ 4\text{Al} \\ 4(\text{OH})+2\text{O} \end{array} \right]$	$\left[\begin{array}{l} 2(\text{OH})+4\text{O} \\ 4\text{Al} \\ 2(\text{OH})+4\text{O} \end{array} \right]$	Unit Cell
(tetrahedral) silicate layer	$\left[\begin{array}{l} 2\text{Si} \\ 6\text{O} \\ 2\text{Si} \\ 2(\text{OH}) \end{array} \right]$	$\left[\begin{array}{l} \cdot \\ \cdot \\ 4\text{Si} \\ 6\text{O} \end{array} \right]$	

Both the above formulas are idealized. Aluminum may be replaced by magnesium and certain other ions, and, to a lesser extent, silicon may be replaced by aluminum. The replacement of one ion by another of similar size is termed isomorphous replacement. It is to be understood that this substitution occurred at some time during the past history of the clay and the ions so substituted are now an essential part of the crystal lattice.

Isomorphous replacement of one ion by another of lower valency has the effect of making the lattice negative. To become electrically neutral, the lattice must attract positive ions. In general these ions are held externally to the lattice and between successive crystal plates. They are referred to as exchangeable ions since they can be replaced by treatment with a solution containing other positive ions. Water also is held

between the crystal plates. If bentonite is placed in water the clay is seen to swell. This swelling is due to water molecules penetrating between successive layers and forcing them apart.

Ross and Hendricks (19),(22) suggested the following formula for montmorillonite:



In the above formula, magnesium has replaced part of the aluminum and the unbalance of charge is offset by attraction of sodium ions. Lattice substitution may not be the only cause for base exchange (9), however, it provides a workable explanation for the observed facts.

Smith (21) studied base exchange reactions of bentonite with salts of organic bases and observed that when the base exchange sites were saturated the complex often flocculated. Giesecking (7) and, more recently, Jordan (13),(14) investigated the physical changes accompanying amine-clay reactions.

Around 1940 Hauser and Leggett (10) were seeking an explanation for the discoloration of white sidewall tires. This study resulted in the discovery that there were color reactions between amines and clay. Seventy-seven different nitrogen compounds were tested and it was found that only certain amines of the aniline type produced colors. Since these colored bentonites swelled in water and permitted base exchange it was concluded that this process was not simply base exchange. Hendricks and Alexander (11) suggested that the color was due to oxidation of a small

amount of the amine to the semiquinone form. Later Ross (18) proposed the use of benzidine and o- and p-phenylenediamine as field tests for clay minerals.

Slabaugh (20) has shown that the exchangeable ion will react with acyl halides forming compounds similar to mixed anhydrides. Bart and Gusman claimed the esterification of bentonite with alkyl halides, although attempts by others to prepare organo-bentonites by this method have failed.

It is well known that organic acids may be esterified by reaction with diazomethane. Berger (1) claimed the esterification of hydrogen bentonite by reaction with an ether solution of this reagent.

Deuel and co-workers (3),(4),(5) attempted to chlorinate bentonite by means of thionyl chloride. This supposedly replaced hydroxyl groups on the silicate layer with chlorine atoms. The bentonite chloride was reacted with organic compounds by methods known to be successful for chlorosilanes.

Spencer and Giesekeing (22) used Deuel's method to produce montmorillonite chloride. This was reacted with phenylmagnesium bromide in an attempt to prepare phenylmontmorillonite.

The work of Berger, and Deuel and co-workers has been challenged by Brown, Greene-Kelly and Norrish (2). The latter investigators pointed out that Berger determined the methoxyl content of the proposed ester without first proving that the product was free of methyl alcohol and ether. They were unable to repeat Deuel's preparation of phenylbentonite. It was pointed out

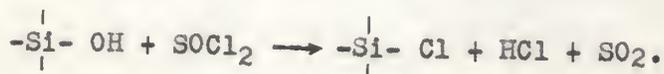
that the (001) spacings of the supposed phenylbentonite were essentially identical with those of hydrogen bentonite. They were able to obtain a similar product only if benzene contaminated with thiophene was used. The conclusion was drawn that the product was not a true compound but merely hydrogen bentonite with sorbed organic material.

EXPERIMENTAL EVALUATION OF BENTONITE CHLORIDE

Raw Wyoming bentonite was purified by preparing a 2 percent suspension of the clay in water and allowing the coarser particles to settle over a period of several weeks. The suspension was decanted off and converted to hydrogen bentonite by passing it through an ion exchange column. The column had been packed with permutit Q, a sulfonic acid resin exchanger, treated with 100 milliliters of 10 percent sulfuric acid, and washed with water until the effluent was neutral to litmus.

The suspension of hydrogen bentonite was evaporated to dryness in a 100°C. oven, ground to pass a sixty mesh sieve, and dried overnight at 105°C. This dry hydrogen bentonite was refluxed for two and one-half hours with redistilled thionyl chloride.

According to Deuel, the reaction was probably:



Excess thionyl chloride was removed by decantation and subsequent distillation under reduced pressure. The resulting product was

dried at 95°C.

Spencer and Giesecking (22) prepared bentonite chloride in a similar manner and reacted it with phenylmagnesium bromide. The reaction supposedly proceeded as indicated by the following equation:



These workers studied the distribution of the product between two immiscible liquids, but did not report the carbon content.

This work was repeated by the writer and a dark brown product was obtained. The material was analyzed for carbon by the standard combustion method and three determinations gave 4.7 percent, 5.2 percent, and 6.3 percent carbon. The product was extracted for twenty-four hours with n-hexane and dried overnight at 85°C. Carbon was determined on this repurified sample and two determinations gave 4.54 percent and 4.44 percent carbon.

The decrease in carbon content following extraction showed that the purification methods employed by Spencer and Giesecking were inadequate. It was also noted that after extraction the dark brown color of the sample gave way to a nearly black color. The presence of free carbon was thereby strongly indicated. This point was emphasized further by the fact that Spencer and Giesecking were unable to remove all the organic radicals from the product by cleavage with boiling 35 percent potassium hydroxide. The amount of organic matter removed was not stated and no cleavage products were identified. These inconsistencies,

coupled with later findings, have led to the belief that the proposed phenylmontmorillonite probably consists of hydrogen bentonite with condensed organic matter.

In order to study the chemical properties of bentonite chloride an attempt was made to react it with other organic compounds. Reaction with sodium salts, through elimination of sodium chloride appeared promising. Sodium phenoxide was the first such compound tested.

One gram of sodium phenoxide was added to two grams of bentonite chloride suspended in carbon tetrachloride and the mixture refluxed for three hours. At the end of this time the product was separated, dried at 100°C ., and found to contain only faint traces of carbon.

Sodium benzoate was tried also. In this case two grams of bentonite chloride were suspended in dioxane and an excess of sodium benzoate added. The resulting mixture was refluxed for three hours and the product extracted with ether. A small amount of carbon was shown to be present by charring the dry sample; however, blank determinations indicated moderately strong adsorption of dioxane and ether by the bentonite. A comparison of the char tests revealed no substantial difference.

The sodium alcoholates represent a class of compounds somewhat different from those previously tested. For this reason sodium ethoxide was prepared and the bentonite chloride treated as described below.

An excess of sodium ethoxide in ethanol was added to two

grams of bentonite chloride and the mixture was refluxed for three hours. The product was extracted with ether and dried. Again a comparison of the char test with that of a blank indicated no favorable results.

One further reaction was attempted. In this case a carbon tetrachloride solution of two grams of phenol was added to two grams of bentonite chloride and the resulting mixture was refluxed for two and one-half hours. The product was then extracted with carbon tetrachloride and dried for forty-eight hours at 85°C. A sample of hydrogen bentonite was treated similarly. Both samples darkened during refluxing and gave positive char tests. Carbon was determined by combustion, however both samples gave essentially the same result (0.74 percent and 0.76 percent carbon).

It has been shown that no well defined compound resulted from the interaction of bentonite chloride with a variety of organic compounds. The failure of this series of reactions has forced the conclusion that bentonite chloride does not exist. The proposed bentonite chloride is probably hydrogen bentonite with adsorbed thionyl chloride.

DIRECT SYNTHESIS

Halogenation

At present the only organic bentonite derivatives which have been reported and remained unchallenged are those in which

reaction is believed to have taken place at the base exchange site. This type of reaction obviously is limited to the base exchange capacity of the clay.

As noted earlier, Deuel attempted to chlorinate bentonite by means of thionyl chloride and thereby convert it into a substance similar to silicon tetrachloride. The greatly enhanced reactivity of bentonite expected from such a conversion prompted attempts to halogenate the clay by using the free halogens chlorine, bromine, and iodine.

A concentrated solution of iodine in carbon tetrachloride was added to bentonite and the mixture allowed to stand at room temperature for several weeks. Samples were removed at intervals and freed of iodine and solvent by evaporation. The products were then hydrolyzed with water and tested for acidity with litmus. Hydrolysis of a silicon-halogen bond replaces the halogen with hydroxyl and eliminates hydrogen halide. Where X is a halogen, the reaction may be represented as follows:



No positive tests were obtained.

In the case of bromine, seven solutions of bromine in carbon tetrachloride were prepared varying in concentration from 5 percent to 100 percent bromine. Bentonite was added to each of these solutions and allowed to remain at room temperature for several weeks. As in the case of iodine, samples were removed, freed of halogen, hydrolyzed, and tested for acidity. After two

months contact there was no indication of reaction.

Chlorine, being gaseous, required different methods of treatment. In order to insure maximum contact of chlorine and bentonite, the bentonite was suspended in carbon tetrachloride and chlorine was bubbled through the suspension. Other organic solvents also were used as suspending agents, although the complications introduced by chlorinated organic products forced the writer to return to the use of carbon tetrachloride. Chlorinations were conducted at room temperature in the early part of the work and later at somewhat higher temperatures. Unfortunately, the use of carbon tetrachloride as a suspending agent limited the maximum temperature to the boiling point of that substance (77°C.). Products were tested in the same manner as described for bromine and iodine. The chlorinated products were acidic to litmus, but not sufficiently acidic to suggest further study.

Reaction with Sodium

Both Berger, and Deuel and co-workers attested to the correctness of the Edelman structure of montmorillonite. Even though the evidence presented by these workers has been questioned, many investigators prefer the Edelman structure. It has been pointed out that Edelman proposed a surface of hydroxyl groups while Hofmann suggested a surface of oxygen atoms. The Edelman structure pointed to a possible reaction with sodium. It was reasoned that if hydroxyl groups were present it might be

possible to replace the hydroxyl hydrogen with sodium. This type of substitution has often led to interesting and useful compounds. Further, the success of the experiment would have provided chemical evidence favoring the Edelman structure.

Four grams of bentonite were suspended in carbon tetrachloride and approximately two grams of sodium, cut into small pieces, were added. The mixture was refluxed for five hours and at the end of this time the sodium was removed mechanically. The treated bentonite was then suspended in bromobenzene and refluxed for three hours. Excess bromobenzene was decanted off and the product extracted with ether. A char test showed only faint traces of carbon.

The (001) spacing was measured by X-ray analysis and was found to have a value of 9.932 Å. Untreated bentonite had an (001) spacing of 11.672 Å.

Reaction with Cyanuric Chloride

Some compounds with active halogen have been shown to react with bentonite (20), (3). In general these reactions proceed through loss of HX or NaX , where X is a halogen. The chlorine atoms of cyanuric chloride are intermediate in activity between alkyl chlorides and acyl chlorides. Therefore it seemed a promising compound to test.

The cyanuric chloride was received in a rather impure form. Attempts to recrystallize the compound were only moderately successful, however sublimation under reduced pressure gave a clean

white solid with the proper melting point.

In the early work hydrogen bentonite was suspended in carbon tetrachloride and an excess of cyanuric chloride added. The resulting mixture was then refluxed for two or three hours and the product separated by centrifugation. Char tests indicated the presence of carbon. The reaction may be indicated as follows:



In order to establish the composition of the products various analytical methods were employed. Attempts were made to hydrolyze the products with hot water and titrate the hydrochloric acid formed, following the course of the reaction with a pH meter. However the pH meter fluctuated widely and there was some uncertainty regarding the number of chlorine atoms hydrolyzed so this method was abandoned.

It was learned that sodium ethoxide reacts readily with cyanuric chloride replacing all the chlorine atoms through the formation of sodium chloride.



Unfortunately, sodium ethoxide also reacts with carbon tetrachloride. This feature of the analysis made it necessary to replace carbon tetrachloride with acetone in the original reaction mixture. Sodium ethoxide used in the analysis was prepared by dissolving two grams of sodium in 100 milliliters of absolute alcohol.

All attempts to employ common volumetric procedures for the

determination of the liberated sodium chloride were unsuccessful. This was largely due to the turbidity produced by oxidation of the excess sodium ethoxide. Gravimetric methods were found to be applicable provided a blank was run to establish the amount of foreign matter produced by the sodium ethoxide.

Prior to analysis, samples were dried for four hours at 76°C. in a vacuum oven. Notwithstanding this treatment some cyanuric chloride may have remained adsorbed. Since there was no obvious method for determining if one, two, or all three of the chlorine atoms were replaced, all chlorine was calculated as cyanuric chloride and subtracted from the total amount of cyanuric chloride found by carbon analysis.

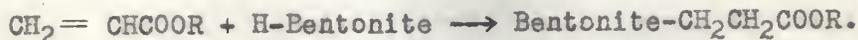
An attempt was made to determine nitrogen by the Kjeldahl method. Unfortunately, the cyanuric chloride sublimed before it could be digested in sulfuric acid.

The carbon content was determined by combustion. After allowance was made for adsorbed solvent, it was possible to calculate the extent of reaction. Two reactions under slightly different conditions showed 48.5 milliequivalents of cyanuric chloride per 100 grams of bentonite and 66.5 milliequivalents of cyanuric chloride per 100 grams of bentonite.

Reaction with n-Butyl Acrylate

Hydrogen bentonite is somewhat analogous to an inorganic acid. Since some inorganic acids add to olefinic double bonds it was suggested that hydrogen bentonite might react similarly

with acrylic esters. Reaction should take place according to the following equation:



In order to test this hypothesis hydrogen bentonite was suspended in a carbon tetrachloride solution of n-butyl acrylate and the mixture was refluxed for about three hours. The product was washed five times with hot carbon tetrachloride, extracted for twenty-four hours with carbon tetrachloride in a Soxhlet extractor and dried overnight in a 76°C. vacuum oven. A char test showed the presence of carbon.

A variety of substances were tested for possible catalytic effect on the reaction. For every two grams of hydrogen bentonite and ten milliliters of n-butyl acrylate, the following amounts of catalyst were used: concentrated sulfuric acid, two drops; sodium hydroxide, one pellet; sodium carbonate, 0.1 gram; Armeen 14D (a fourteen carbon amine), 0.1 gram; and concentrated ammonium hydroxide, one milliliter.

Three principal analytical methods were employed to establish the composition of the bentonite-acrylate complex. The first of these involved determination of the amount of unsaturation in the complex. This technique was used to provide information regarding the amount of unreacted acrylate remaining on the bentonite.

In this method 0.2000 grams of the complex were placed in an iodine flask and 25 milliliters of a standard solution of

bromine in carbon tetrachloride added. The flask was then allowed to stand in the dark for one hour. At the end of this time it was removed and 10 milliliters of potassium iodide solution (150 grams KI per liter of solution) added. The resulting mixture was then diluted with 50 milliliters of water and titrated with standard sodium thiosulfate to the starch-iodine end point. The reaction may be represented as follows:



In order to insure the validity of this method, the time of standing was increased from one hour to thirteen hours. The results obtained by this modification were essentially the same as those obtained previously.

The total amount of carbon was determined by combustion. Even though carbon tetrachloride is rather weakly adsorbed by bentonite, a blank was run and the correction applied to all results. The amount of complex formed and the catalyst employed are presented in the following table.

Catalyst	Amount of acrylate in meq. per 100 g. bentonite
none	45
NaOH	57
Na ₂ CO ₃	64
Armeen 14D	112
NH ₄ OH	243
H ₂ SO ₄	13

The infrared-spectrum of the complex was studied also. Spectra were obtained for pure hydrogen bentonite, pure n-butyl acrylate, the bentonite-acrylate complex and a mixture of hydrogen bentonite and n-butyl acrylate. It was hoped that complex formation would cause the disappearance of the peak due to the acrylate double bond. Unfortunately however, the spectrum of hydrogen bentonite also has a maxima at 6.025 microns. Although this point could not be evaluated, it was noted that the carbonyl band appearing at about 5.8 microns was intense in the pure n-butyl acrylate, but either greatly diminished or entirely absent in the complex and mixture.

DISCUSSION OF RESULTS

Results obtained by direct halogenation showed that, under the conditions employed, neither bromine nor iodine reacted with bentonite. There were two possible explanations of the reaction with chlorine. The acidity of the hydrolyzed product could have resulted from adsorbed chlorine, in spite of efforts to remove it, or the reaction may have taken place to a small extent. It is possible that the reaction temperature was too low to effect a conversion. A chlorination in the range of 300° to 400°C. should prove very interesting.

Reaction between metallic sodium and bentonite was unsuccessful. The successful substitution of sodium for hydroxyl hydrogen would have provided positive experimental evidence favoring the Edelman structure. However, the failure of the

experiment cannot be interpreted as favoring either structure. Evidence was of two kinds; chemical and physical. The lack of carbon in the product after refluxing with bromobenzene indicates that no reaction took place. Further, the decrease in (001) spacing corresponds to nearly complete dehydration of the bentonite. This latter piece of information can be explained using either structure as a model. If the Hofmann structure is assumed then no reaction between sodium and bentonite would be expected and the decreased (001) spacing can be explained simply as removal of interlayer water. If the Edelman structure is correct then reaction probably took place by removal of water from two adjacent hydroxyl groups, leaving a structure somewhat similar to that proposed by Hofmann.

The reaction between cyanuric chloride and hydrogen bentonite has been investigated by two analytical techniques. Since some cyanuric chloride may have been held by simple adsorption it was impossible to calculate if one, two or all three chlorine atoms entered into reaction. After due allowance was made for adsorbed solvent, the carbon content was a measure of the total amount of cyanuric chloride present. The subtraction of chlorine as cyanuric chloride is justified since the initial number of chlorine atoms less the number present after reaction is a direct measure of the extent of reaction. This measure follows regardless of the mode of reaction. After all the above corrections were made a substantial amount of carbon remained. Both the samples reported were prepared using an excess of

cyanuric chloride, however the one showing the larger amount of carbon was heated to a somewhat higher temperature.

It has been shown that hydrogen bentonite reacted with n-butyl acrylate. The reaction probably took place by addition of hydrogen bentonite to the acrylate double bond.

A comparison of catalyst used and amount of complex formed revealed that basic substances favored the reaction while acidic substances tended to repress complex formation. In spite of this general trend, certain anomalies exist. Undoubtedly the Armeen 14D formed a complex with the clay thus invalidating the gravimetric factor. Apparently some side reaction took place in the case of the ammonium hydroxide catalyzed reaction since the amount of carbon found is over two times the base exchange capacity of the clay.

The conflicting maxima noted in the infrared data has greatly limited its usefulness. However the disappearance of the carbonyl band in the complexes and mixture is worthy of note. This may be the result of hydrogen bonding or it may be more fundamentally associated with the reaction. The fact that the mixture of n-butyl acrylate and hydrogen bentonite shows this repression points to the first explanation. However, it is also possible that reaction took place during the preparation of the sample for analysis.

Because of the complicating factors noted above, the infrared data is difficult to evaluate, however all the chemical information points to a compound formation.

In view of the above work several new reactions suggest themselves. Hydrogen bentonite might react with alkyl cyanates (RNCO) or alkyl thiocyanates (RNCS). Also, the field of organo-metallics has not been investigated. Compounds of chromium with attached phenyl groups are known and might well provide a new avenue of approach to the problem of organo bentonite synthesis.

SUMMARY AND CONCLUSIONS

The origin and mineralogy of bentonite has been traced briefly. Consideration has been given to the proposed structures for montmorillonite and base exchange properties have been explained in terms of isomorphous substitution in the clay lattice.

The early discovery of color reactions between clays and amines has been indicated and the subsequent exhaustive study of amine-clay reactions mentioned. A variety of other organic bentonite derivatives also have been described.

Recent work by Deuel and co-workers, and Spencer and Giesecking has been given special attention. It has been shown that there is considerable evidence against the existence of bentonite chloride. It is concluded that this substance does not exist.

Attempts to synthesize halogenated derivatives of bentonite were unsuccessful. However, a possible high temperature chlorination has been suggested.

Under the conditions employed, sodium did not react with bentonite. The failure of this experiment has been interpreted

as favoring neither the Edelman nor the Hofmann structure of montmorillonite.

Cyanuric chloride has been shown to react with hydrogen bentonite by the elimination of hydrogen chloride. The number of chlorine atoms per cyanuric chloride molecule entering into reaction was not determined.

Analytical data indicated that reaction took place between n-butyl acrylate and hydrogen bentonite. The analogy has been drawn between this reaction and addition reactions of inorganic acids and unsaturated organic compounds.

It was concluded that the reactions between hydrogen bentonite and n-butyl acrylate, and hydrogen bentonite and cyanuric chloride resulted in the formation of new organic bentonite derivatives.

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Bentonite is the term applied to a clay material consisting chiefly of the mineral montmorillonite. Chemically it may be considered a hydrous aluminum silicate. Two different structures have been proposed for montmorillonite. Both structures show that montmorillonite is a layer type mineral consisting of an aluminum hydroxide (gibbsite) layer bound between two silicate layers. From the standpoint of this work, the only significant difference between the two structures is that Hofmann and co-workers believe the surface of the clay laminae to consist of oxygen atoms whereas Edelman and Favejee favor a surface of hydroxyl groups.

Isomorphous substitution may occur to some extent in both the gibbsite and silicate layers. This replacement may lead to a net negative charge on the clay lattice. As a result the clay lattice must attract external positive ions. These positive ions have the property of being exchangeable for other positive ions and consequently are called exchangeable ions. The ability of a clay to exchange one ion for another is referred to as its base exchange capacity. The ion occupying the base exchange site may be either inorganic or organic.

Bentonite-amine compounds probably have been studied more than any other class of organic bentonite derivatives although many other organo-bentonites have been described. Most of these compounds have resulted from either direct addition reactions or by elimination of hydrogen halide or metal halide. In this respect a reaction proposed by Deuel and co-workers is unique. It

was claimed that thionyl chloride replaced hydroxyl groups on the clay lattice (Edelman structure) with chlorine atoms. These workers reported that reaction took place between the resultant bentonite chloride and a variety of alcohols and phenol. The writer was unable to repeat the reaction with phenol. No alcohols were tested.

Spencer and Giesekeing used Deuels method to prepare montmorillonite chloride and claimed the synthesis of phenylmontmorillonite by means of a Grignard reaction. The data presented by these investigators is incomplete and an attempt by the writer to repeat their work has led to a product of questionable composition.

An unsuccessful attempt was made to react montmorillonite chloride with other organic compounds. It has been concluded that montmorillonite chloride does not exist and that what Deuel thought to be montmorillonite chloride was actually hydrogen bentonite with adsorbed thionyl chloride.

The writer has made several attempts to halogenate bentonite with the free halogens, chlorine, bromine, and iodine. None of the experiments were successful.

An attempt was made to react metallic sodium with bentonite, however this only resulted in the dehydration of the clay.

The first successful synthesis resulted from the interaction of hydrogen bentonite and cyanuric chloride. This is the type of reaction, mentioned earlier, in which hydrogen halide is eliminated. The extent of adsorption of both solvent and cyanuric

chloride was determined and an appropriate correction made.

Hydrogen bentonite also was found to react with n-butyl acrylate. In this case reaction probably took place by direct addition. Again a correction was applied to account for adsorbed organic matter.

The reactions involving cyanuric chloride and n-butyl acrylate are believed to constitute new organo-bentonite derivatives.