Victor F. B. de Mello

FINAL REPORT

PHASE I

SOIL SOLIDIFICATION PROJECT

Submitted to

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PART I LABORATORY INVESTIGATIONS AND RECOMMENDATIONS

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PREFACE

The Program and Contract

The soil solidification program of the U.S. Engineer Board, as outlined in a circular letter dated 27 December 1945, divided the work into four classes as follows: 1) Chemical 2) Electrical 3) Thermal 4) Others. The aforesaid letter invited a proposal from the Institute, stating under what conditions the work would be undertaken. Such a proposal was submitted and accepted by the Army, and contract number W-44-009-eng-408 was signed on 18 June 1946. The proposal by the Institute was for research on the first class, chemical solidification. The contract was for one year commencing in August, 1946, but was later extended to terminate on 15 March 1948.

The work was undertaken with the understanding that the research would be in three phases, the first phase to be a period devoted to a "paper study" of literature on previous research of a similar nature, and of preliminary experimental investigations. It is this phase that is covered by the above-mentioned contract and which is covered by this report. Subsequent phases are as follows: 2) A period devoted to exploratory experimental studies of the effects of various chemicals on soil solidification; 3) A period devoted to extended laboratory soil-chemical tests.

Organization

It was recognized from the first that this project would be partly of a chemical and partly of an engineering nature, and, therefore, a steering committee consisting of members of the Departments of Civil and Sanitary Engineering and Chemical Engineering was made up. This committee consists of:

Professor D. W. Taylor, Chairman
  Associate Professor of Soil Mechanics
Professor A. J. Bone
  Associate Professor of Highway and Airport Engineering
Professor E. A. Hauser
  Associate Professor of Chemical Engineering
Professor E. B. Millard
  Professor of Physical Chemistry
Professor C. N. Sawyer
  Associate Professor of Sanitary Chemistry
Dean T. K. Sherwood, ex officio
  Dean of Engineering
Professor J. B. Wilbur, ex officio
  Professor of Civil Engineering; Head of Department
  of Civil and Sanitary Engineering

The work was set up under the technical supervision of Professor D. W. Taylor for civil engineering and Professor E. A. Hauser for chemical research. As the work to date has been entirely of a chemical nature, all of the technical supervision has been that of Dr. Hauser; he has also been the source of all of the ideas for the investigations.

The staff of the project has grown throughout the period covered by this report and at present is as listed below, together with the starting date for each:

Mr. V. F. B. de Mello, Research Associate
1 October 1946
Mr. R. S. Hess, Research Associate
15 February 1947
Miss C. A. Sturenburg, Research Assistant
15 July 1947
Mrs. M. Pomeroy, Research Organic Chemist
1 December 1947

Preparation of Report

This report has been prepared by Victor F. B. de Mello, Robert S. Hess, and Constance A. Sturenburg under the technical supervision of Professor E. A. Hauser and the administrative supervision of Professor J. B. Wilbur and Professor D. W. Taylor. The discussion of the literature review (Part II) was written up by Victor F. B. de Mello.

LABORATORY INVESTIGATIONS

Summary

This report describes the preliminary laboratory investigations which have been undertaken to determine the most promising types of agents for chemical soil solidification. The major objective at this time has been to find what classes of chemicals will give the action desired; later work will attempt to find the specific agents which can be most easily and economically applied, giving the strongest product. In this phase of the work, practicability of application and economy were not to be controlling factors, although in the later phases these considerations should play a leading role.

Three classes of agents have been investigated to date, clays, silicates, and certain synthetic resins, each of which has advantages and disadvantages which will be discussed in more detail below. None of these fields has yet been exhausted; there remain many methods of utilizing these agents which require further study.

While no completely satisfactory solidifying agent has yet been found among the chemicals tried, a large amount of valuable information has been obtained on the properties of the agents alone and admixed with sand. It is believed likely that there are reagents of the general type considered that will furnish satisfactory solidifying treatments that can be developed through further study along the lines already undertaken.

Introduction

The problem of soil solidification is of great importance in many fields. Besides its obvious military applications, it is of much interest in such civilian uses as oil-well drilling, road-building, air-field construction, building and other sub-foundations, etc. Consequently, much work has been done previously to find a solution to this problem. A thorough survey of the literature pertaining to previous investigations and a bibliography are submitted together with this report. Most of this previous work was attacked from a civil engineering point of view, with little or no attention being paid to the chemical properties of the soils. While it is not intended to detract in any way from the contributions, past and future, of civil engineers to this problem, it is believed that no satisfactory solution will be reached without the aid of the chemists, especially colloid chemists.

When the project was started at the Massachusetts Institute of Technology, it was immediately realized that the first problems involved would be colloid-chemical, both in regard to the study of soils and their behavior, and in the use of a chemical agent as a solidifier. Therefore, much work has been devoted to a study of the colloidal properties of clays and soils, most of the information being derived from the literature pertaining to this field.

As the contract specified that this phase of the investigations was to be conducted "with the view of determining a recommended program involving the trial, modification and/or development of chemical agents for use in the solidification of soils," the laboratory work has been limited to that necessary for giving general indications or for achieving better understanding of the properties of the reagents used. Tests on solidified soil samples were of a qualitative nature rather than quantitative, only sufficiently accurate to determine whether a particular reagent showed any promise as a solidifying agent.

It is believed that for miliatry uses, the desired agent should be one which can be easily applied; the most satisfactory method of application has been assumed to be by spraying. The ideal goal towards which the work has been aiming is an agent which can be applied by spraying from the air. If this is achieved, it will be possible for an area to be solidified without having to land any personnel in the area. While this goal is the ideal, it is not to be felt that any results short of this indicate failure; all agents which show promise are being investigated whether they are suitable for spraying or not.

It is perhaps advisable to attempt a definition of an "ideal" solidification treatment. Such a treatment should completely submerge the natural physical properties of the soil; even more ideally, the solidifying agent should be universally applicable. It would then be possible to treat any soil without preliminary analysis. The above statements may appear to commit this project at M. I. T. to achieving results of the order of "ideal solidification". This is not so; the ideals are described not because it is believed that they are easily obtainable, but because it is felt necessary to establish a standard for evaluation.

Description of Materials

In order to simplify the problem by eliminating from present consideration all the complex variables that appear in average soils, it was decided to limit the preliminary stages to the use of clean sand as the soil to be solidified. This decision, taken with a view to best long-range and over-all progress, is, nevertheless, fully practical in its scope, since the solidification of sands is a problem of considerable importance. The sand chosen for this purpose was Standard Ottawa Sand, a pure silica sand; run-of-mine grade was used which passed 20 mesh and was retained on 200 mesh sieves. The approximate grain-size distribution is shown in Table I.

The bentonite used in these experiments is a Wyoming bentonite, 350 mesh. The silicates and resins are commercial grade, and all other chemicals are C. P. Reagent grade.

TABLE I

Sieve Analysis of Sand

Sieve Number	Size of Mesh in mm.	% of Sand Retained
20	0.833	0
28	0.589	7
35	0.417	42
48	0.295	29
65	0.208	10
100	0.147	6
150	0.104	3
200	0.074	3
		100%

Laboratory Testing Procedures

The testing procedures used to date are admittedly over-simplified, but they serve the purpose of giving indications of relative success or failure without spending too much time on refined tests. It is possible to determine to a reasonable degree of accuracy whether a given agent shows any promise or not from these simple, rapid tests. Those which have shown promise will be given more thorough investigation in the following phases of the project.

Test specimens were prepared in cylindrical molds about 1½ inches in diameter and about 3 inches tall. The sample was put in these molds and then tamped by means of a light piston about one inch in diameter. No standard compacting procedure was used, but it is estimated that all samples received reasonably similar compaction. This light tamping is not believed to have much effect on the compressive strength of the samples except insofar as air pockets are eliminated.

The strength of the samples was determined by simple, unconfined compression; this method is a rapid, reliable method of determining the shearing strength. While objections may be raised to the use of compression tests with a constant rate of strain on brittle samples, it is believed that for comparative purposes in assessing the relative merits of various solidifying treatments the compressive strengths obtained can be relied on. For indication of absorption or capillary rise of water, the samples were immersed in water, either completely or to a depth of about one centimeter. Observations were made by visual examination, and the samples were then subjected to unconfined compression tests when wet and when redried. In all tests, a ratio of about 98 per cent sand to two per cent of bonding reagent was used, except as otherwise indicated.

Bentonite as a Bonding Agent

The use of bentonite was suggested by the fact that it exhibits very good bonding power when dry, and that it may be made water-resistant by means of base-exchange reactions. The ability of bentonite to exchange cations is a well-known phenomenon which has had sufficient application to indicate its possibility for the purposes of this investigation. As the mechanics of base-exchange are explained in the section of colloid chemistry in Part II, it is not believed necessary to explain them here.

Tests were first conducted on simple, inorganic cations, such as K^+, Pb^{++}, Ca^{++}, Mg^{++}, Al^{+++}, etc. Sand was mixed with an 8 per cent suspension of bentonite in the ratio of 2 per cent dry bentonite to 98 per cent dry sand. This was then molded, dried, and the exchange solution poured through. The sample was then redried and tested. The results obtained showed that these reagents were unsatisfactory for producing the desired results. The dry samples were considerably weaker than the samples made with unexchanged clay, and the wet samples showed no strength at all, disintegrating under their own weight.

It was then believed that more favorable results might be obtained through the use of more complex cations. Two classes of such cations are being considered:

1) Those containing a hydrophilic, inorganic component, chemically combined with a hydrophobic organic component which preferably contains a long, paraffinic chain.

2) Those containing a hydrophilic, inorganic component, chemically combined with an organic component which is capable of polymerization.

In the first type, exchange will take place in such a manner that the inorganic component will be oriented towards the clay particle, and the hydrophobic, organic component will be oriented outwards. Thus, protection against water would be furnished by the water-repellent characteristics of organic long-chain structures. Some preliminary work has been undertaken on the use of this type of exchangeable cation, and is described below.

Exchange of the second type will take place in a similar manner to the first, but the organic radicals will then be polymerized. Thus the water-resistance is furnished by a chemical bonding of the clay particles, rather than by a water-repellent surface on the individual particles. By means of this type of reaction, many clay particles can be chemically joined to form one large particle which is quite rigid and unaffected by wetting. The work which has been done on this type is also set forth below.

Type 1

The chemicals of type 1 fall into two groups, organic complexes of polyvalent metals and the organic ammonium compounds; only the latter have been tried to date. The ammonium compounds may be divided into three classes: amines, amides, and quaternary salts. It was expected from their chemical composition that the amines and quaternary salts would base-exchange and that the amides would not. These expectations were borne out by experimental results. The amines and quaternary salts tried gave favorable indications and will be investigated more thoroughly in a future stage of the project.

Several problems arose in connection with the use of these reagents. A major difficulty is that the application requires wetting and drying twice, and that the samples showed poor strength characteristics while wet until after the second drying operation. Another source of trouble is the low degree of penetration of the reagent into both the sample and the clay agglomerates within the samples. When samples were exposed to the exchange solution, this penetrated the sample only slowly, and apparently reacted only with the surface layer of the clay agglomerates. The surface of the bonding clay agglomerates having been rendered hydrophobic by the base-exchange treatment, capillary rise of water in the interstices between the sand particles is effectively inhibited. It is believed, however, that the molecules of water vapor from humid air are not prevented from entering the clay agglomerates, and swelling and softening the unexchanged clay within. Penetration studies that are now being conducted with the use of wetting agents, etc., as described on page 10, are expected to yield results that will be useful in overcoming some of these difficulties.

The samples were prepared by mixing a bentonite suspension with sand, using a ratio of two per cent of dry clay to ninety-eight per cent of sand. The mixture was molded as previously described and allowed to dry. The exchange solution was then poured through and the sample again allowed to dry under atmospheric conditions. In all tests, it was found that no appreciable strength is shown until drying is essentially complete. Tests also showed that if the clay is exchanged prior to admixture with sand, no bond results. The bond must apparently first be formed with sodium clay, and then protected by base-exchange.

It was observed that, if clay is exchanged in suspension, filtered, washed, and allowed to dry, it forms a hard, rock-like mass which is not wetted by water even after prolonged submergence. This would indicate the possibility that clays and clayey soils may be solidified by direct treatment with quaternary salts and possibly other base-exchanging reagents, if a suitable mixing procedure is employed so as to achieve complete exchange. In arriving at this conclusion, indications were obtained through the use of two extreme types of clay minerals; bentonite and kaolinite.

Type 2

Base-exchange seems to be the only suitable chemical reaction for modification of clays with reference to soil solidification, and the use of complex organic cations which may be polymerized subsequent to base-exchange offers the best promise for the solidification of clayey soils. Such a base-exchange reaction must employ aqueous solutions; consequently it would be desirable, or even necessary, to achieve the polymerization of the base-exchanged complex organic radical in the presence of water, and at atmospheric temperature and pressure.

Preliminary work has been done on the base-exchange of a commercial Wyoming bentonite with concentrated solutions of calcium methacrylate and lead acrylate. These reagents are for the present being used as representative of the whole group; some study will later be devoted to a comparison of the advantages and disadvantages of the various specific reagents. The investigation of the possibility of effecting the necessary polymerization in an aqueous medium has been initiated with the use of what is termed "reduction-activation" catalysis. Although the work on these polymerization studies has just started, indications of promise have already been obtained. Attention is now being devoted to the development of a suitable method for determining the extent and effectiveness of the polymerization achieved in various runs, so that the conditions necessary for effecting the optimum amount of long-chain polymerization may be ascertained.

Sodium Silicate as a Bonding Agent

The use of sodium silicate in stabilizing and solidifying soils has been known for some time. The most successful means of application in which the reagents are forced into the ground under pressure was first reported some time ago. This procedure has been applied mainly in subsurface work to strengthen soils beneath heavy structures, rather than for surface solidification. Investigators who attempted surface solidification, found that the reaction product was adversely affected by water. It is believed that protection from water can be achieved through base-exchange of the sodium silicate after admixture with the sand. Base-exchange prior to admixture is unsatisfactory, as the bonding strength cannot then be obtained; this has been confirmed by our experiments.

Many metallic salts were used to determine the most effective cations for this exchange reaction. The most promising were lead and calcium, while many others gave somewhat poorer results. Those that resulted in much weaker samples included aluminum, magnesium, nickel, zinc, and zirconium. In using lead and calcium, it was noticed that the acetate and chloride respectively yielded good results, while the nitrate did not. This indicates that the anion also exerts some influence on the reaction; this anion influence will be studied further in the next phase of the work.

Test specimens made with these reagents showed compressive strengths of the order of 500 pounds per square inch when air dried; oven dried samples gave still higher results. Samples which were wetted after drying lost a major portion of their strength. On redrying, only a fraction of the original strength was regained; this strength showed no relation to the original dry strength, but was three to five times the wet strength.

In testing this method of solidification, it was noted that the higher concentrations of the exchange solutions yielded the better results, saturated solutions being most satisfactory. These results may be attributed to two factors: the mass action effect of high concentrations may be of some importance, and the tendency for the reacting solutions to dilute and wash out the silicate is lessened with higher concentrations.

Ethyl silicate has been tried in place of sodium silicate. While a gelatinous precipitate is obtained when a concentrated solution of hydrochloric acid is added, there is no bonding or adhesive power exhibited by the precipitate.

The method of preparing samples consisted of mixing the silicate thoroughly with sand, and then pressing the mixture into molds. The exchange solution was then poured through; immediately on contact of the exchange solution with the silicate-sand mixture, a hard, abrasion-resistant mass was formed. The major advantage of this method is the instantaneous setting. Another beneficial factor is the ease of application, since, although it has not yet been shown that the silicate can be sprayed on, the exchange solution can probably be thus applied.

As the above-mentioned factors offer much promise for this material, it is believed that it is worthy of more study. There are still some major obstacles to be overcome, such as loss of strength on wetting, but full investigation of these is felt to lie in the development rather than the exploratory phase.

Synthetic Resins as Bonding Agents

In any problem which requires bonding, one of the first class of agents to suggest themselves is that of the synthetic resins. These compounds are finding more and more applications and are considered by some to be practically a universal answer to problems in bonding and fabricating. The major requirements of a synthetic resin in soil solidification are that it must be capable of setting at normal temperature and pressure, and must be in a form which lends itself to application.

Several resins have been tried: Resorsabond, R-11, resorcin--aldehyde condensation products; a melamine alkyd resin; Resinox 426 and Resinox L10060.

Resorsabond

Resorsabond consists of two components: "A", a viscous liquid containing the resorcin; and "B", a powder containing the aldehyde and a filler. The setting time and some of the characteristics of the product can be adjusted by varying the ratio of "B" to "A". Also, varying the proportions of the components of part "B" will affect both the setting time and some characteristics. The mixture of "A" and "B" will set up to a hard, strong resin in about five minutes at 100°C. or from one to three days at room temperature, depending on the proportions used.

Samples were prepared by mixing the resin, containing the recommended ratio of A/B of 5/1, with sand, molding, and allowing to set in air for about 24 hours. This appeared to be sufficient time to allow the resin to set completely.

When submitted to unconfined compression, at two per cent treatment, these samples failed at about 300 pounds per square inch. By increasing the amount of paraformaldehyde in component "B", the strength of the molded samples can be increased. Also, by increasing the ratio of resin added to the sand, the strength increased almost linearly at least up to 5 per cent resin to 95 per cent sand, reaching a value of about 600 psi; higher percentages of resin treatment were not tried.

When the molded samples were immersed in water after setting and allowed to stand, there was a marked decrease in strength. This was accompanied by a coloration of the water, indicating that some of the resin was being washed out. The cause for this is not yet fully understood, but incomplete polymerization is believed to be at least a part of the trouble, since no leaching occurred with oven-dried samples. The heat-cured samples, however, became brittle and lost much of their strength.

Addition of acid to the resin catalyzes the polymerization reaction greatly. By varying the normality and quantity of acid, the setting time can be accurately controlled to vary from immediate setting to several hours. In the samples of resin which were set by acid catalysis, those that set in less than thirty minutes gave off a large amount of heat. The resultant product is very hard--much harder than the plain resin. This procedure has not yet been successfully used in preparing sand-resin samples; the samples prepared so far have been very weak, sand abrading off at the least touch. It is believed that further development may overcome this difficulty. The acidified resin shows no tendency towards weakening or leaching out in water.

Melamine

The melamine resin is an alcohol-modified formaldehyde melamine resin which cures quickly with heat but will eventually cure at normal room temperature.

Samples were prepared by mixing three per cent of the resin with 97 per cent sand and compacting the mixture in the molds by manual tamping; they were then put in a 100°C. oven and allowed to cure for two to three hours. When subjected to unconfined compression, the samples failed at about 800 pounds per square inch.

Upon immersion in water for 48 hours after curing, the samples showed a fifty per cent decrease in strength. The exact cause has not yet been determined.

The setting time at room temperature of the resin may be regulated or accelerated by the adjustment of the pH, and tests are now being conducted to investigate this more fully.

Resinox

The two Resinox resins, 426 and L10060, are very similar in their physical properties as well as in their chemical reactions to Resorsabond R-11. They consist of two components, "A" being the viscous resorcin and "B" the accelerator containing the aldehyde and some inert filler. The procedure for combining the two parts is the same as the Resorsabond; one may also vary the ratio of "A" to "B". The setting time at room temperature is considerably longer though, while curing at 100°C. takes place in less than an hour. A two per cent sample when submitted to unconfined compression fails at about 300 pounds per square inch.

When immersed in water, the air cured samples collapse under their own weight due probably to incomplete polymerization while the oven cured samples maintain a little strength; no leaching occurs with the oven dried samples.

When the reaction is catalyzed with acid, the setting time can be regulated by varying the amount and concentration of the acid. When the catalyzed resin is admixed with sand, the sample does not become as brittle as with the Resorsabond.

Penetration Studies

The problem of penetration is important when one considers spraying or pouring an agent on a beach or field. The ultimate goal would be to achieve a maximum depth with the least amount of material but still obtaining the desired solidification. When considering penetration, e.g., with water, one immediately thinks of ways in which to reduce the surface tension and interfacial tension to obtain greater depths.

Several commercial surface active agents have been tried as well as high molecular weight acids and amines. The most successful of those tried have proved to be Aerosol and Duponol (me) synthetic type wetting agents.

The work done to date on penetration has been done only with water on dry sand by trying the different commercial surface active agents and determining the effect of them at different concentrations. Only the technique of pouring slowly over one spot (avoiding contact with the edges of the container) has been used so that both the penetration and the side distribution could be measured. By using 10cc. of a 0.2 per cent solution of Aerosol, an average depth of 2.5 inches and a side distribution of two inches can be achieved in about five minutes; while using 10cc. of tap water, an average depth of 1.5 inches was obtained.

An apparatus was devised by which the penetration could be measured quickly and easily by slicing the sample in half and in quarters and pushing one part aside after the sample had been saturated with carbon tetrachloride which allowed the sample to hold its own weight but did in no way affect the penetration achieved by the solution under investigation. Several dyes to indicate depth were tried in order to find one that would not wash out when the carbon tetrachloride was added; a few drops of Carter's black fountain pen ink was found to be the most suitable.

RECOMMENDATIONS FOR FURTHER STUDY

Outlined herein is the work to be undertaken during phase two of the project. This work is mostly concerned with the development of agents previously tried which gave promising indications of their applicability. However, as new products and new ideas come to the attention of the project staff, these will also be taken into consideration for incorporation into the work. Such incorporation will be accomplished only after mutual agreement between the contracting parties. It is understood that the work in this phase will not be limited by these recommendations to the exclusion of new ideas which may arise.

As previously pointed out, it is felt that the ideal solution would be to treat the soils in such a way that landing strips and roads passable to heavy equipment could be made, using a reaction which can be instigated without any work having to be accomplished on the soil prior to its solidification. In simpler words, the ideal solution would be to accomplish this by an infiltration process, as for example, by spraying certain chemicals from an airplane. There are yet no data, however, to give assurance that complete achievement of this ideal solution is possible, either from the point of view of degree of solidification obtainable or as regards an ideal method of application such as spraying.

The problem, in any event, involves optimum results relative to two basic phenomena: first, infiltration of the chemicals to be used; second, firm binding action by the chemicals on the soil particles. The work so far has been based on knowledge of the colloid chemistry of soils, including that of quartz sand, with the intention of coating the soil particles with an agent which will not only be firmly attached to the particle, but by further reaction will act as a binding medium for the entire structure. This can be accomplished by using such chemicals as will, by polymerization, form a coherent system. It is already known that clays characterized by a high base-exchange capacity, like certain types of bentonites, can be easily reacted with chemicals which will permit polymerization. It has been found that sea sand can be solidified by the incorporation of polymerizable organic chemicals like resorcinols and other plastics.

The preliminary work has indicated that the basic ideas outlined above are workable, and if fully realized will meet the requirements of the Military Characteristics which are:

1. General:

The end item shall be an element, substance, chemical agent, other material, or method that will expeditiously render soils sufficiently stable to support the emergency operation of airplanes, military vehicles, and amphibious equipment.

2. Detail:

a. Amount of Stabilizing Agent. The amount of the agent, element, or substance necessary to render soils stable should not exceed a small fraction, preferably less than 5% of the weight and volume of the mechanically stabilized thickness of a given soil necessary to support emergency military traffic.

b. Speed of Application and Effect. The agent, element, substance, or method should be readily applicable to the soil to be treated and the stabilizing effect should be accomplished in minimum time.

c. Method of Application. Any mechanical equipment required in applying the agent, element, or substance to the soil shall be suitable for military operations and achieve rapid and economical application. A desirable means of application would be from aircraft or airborne equipment.

d. Deterioration. The agent, element, or substance should be capable of being stored for long periods without appreciable deterioration from weather or temperature changes.

e. Life of Treatment. Soils stabilized or solidified by means of the agent, element, substance, or method should remain stable after application for a reasonable period, preferably two months or more.

f. Injurious Effects. The agent, element, or substance should be free from harmful effects to personnel and equipment during and after application to soil.

The work of the succeeding phase will be conducted in full cognizance of these requirements and will now deal with the following problems:

1) To develop further those chemicals which have so far given the best results, namely silicates, synthetic resins of the low-temperature-setting type, and base-exchangeable clays. All of these have shown promise, but each has certain disadvantages which are covered in the report on the preliminary studies. Further work with these chemicals will be pointed toward overcoming these disadvantages.

2) To study the addition of colloidal clays to types of soils that do not contain appreciable quantities of these clays, such as sea beaches, since there are very definite indications that this addition might be advantageous for the final step of solidification.

3) To study and develop such new materials and ideas as may appear to give good indication of satisfactory application.

4) To study different types of soils in regard to their stabilization by the use of the chemicals which have so far given the best results. In this work the chemical composition of the soil must be known in detail; however, it is not intended to develop new methods of determining this composition.

5) To study systematically the difficulties which certainly will be encountered when treating these various types of soils, to ascertain the reasons for the differences in reactivity and to develop agents which would possibly prove satisfactory for any type of soil which one might conceivably encounter.

6) Since the Military Characteristics require that "soils," without qualification, must be considered, changes of the soil under varying weather conditions must also be studied. It is anticipated that the chief difficulties which will arise in this work will be the accomplishment of sufficient infiltration and bonding action of the chemical used. The achievement of maximum infiltration will, possibly, involve the introduction of dispersing or agglomerating agents.

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PART II LITERATURE REVIEW

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II. Literature Directly Related To Chemical Soil Solidification or Stabilization

III. Fundamental Concepts of Colloid Chemistry and Clay-Mineral Properties

INTRODUCTION

In accordance with the contract of the first phase of the research project on chemical soil solidification, an extensive survey of literature has been conducted. The summary report on this literature review is hereby presented as Part II of the general report covering all the work done in the first phase.

For purposes of this report the literature reviewed is subdivided into two general classes: articles directly relating to chemical soil solidification or stabilization, and literature presenting theoretical concepts of soil and clay properties. These two classes make up Sections I and II of Part II. The literature on fundamental properties of soil and clay is considered most important as a background for the laboratory investigations. The literature directly relating to chemical soil solidification has also been thoroughly reviewed, however, although it had become evident early in the work that for the purpose of the proposed research such literature would not yield very fruitful information.

The literature reviewed does not offer any clear-cut definition of the terms solidification and stabilization as distinct from one another. It is, therefore, thought advisable to include such definitions here:

(a) Solidification is defined as a method of imparting to a soil a strength in no way attributable to the physical properties of the natural soil.

(b) Stabilization is defined as a process of improving the natural soil properties to optimum conditions, and effectively maintaining the soil in that state.

Stabilization may be effected by purely mechanical means such as modification of the particle size gradation and compaction. In the case of clayey soils, most commonly employed is the technique of compacting the soil at an optimum moisture content, and incorporating a waterproofing agent to maintain the soil at this design moisture content; stabilization may further involve adjustments of the Plasticity Index by changing the cations adsorbed on the clay particle. The achievement of a suitable degree of resistance to water-attack is usually the major goal. However, stabilization may also involve consideration of resistance to damage by frost. The specifications for a stabilized soil will thus vary somewhat depending on climatic conditions at the locality.

Solidification involves the use of suitable binding agents. The admixture of Portland Cement with a suitable sandy soil, effecting strengths comparable to poor concrete, is a common example of solidification. No thought has yet been given on this project to the establishment of a definite minimum compressive strength, in pounds per square inch, that will be considered satisfactory for solidified soil; due consideration will be given to the problem when the project develops to the stage of requiring more detailed mechanical testing. For the present, it may be sufficient to indicate that the achievement of strengths comparable to a relatively poor concrete may be called a high degree of soil solidification. Resistance to damage by water and frost is also essential to success in solidification. And finally, from a practical point of view, economy of amount and cost of material used for solidification is highly desirable.

The investigation so far has covered only the search for general types or methods of chemical solidification and stabilization, with practically no thought of refinement of any method. Thus construction procedures and considerations of optimum conditions have been given little attention. Efforts have been made to cover fully all modifications of the chemicals involved in the solidification or stabilization processes reviewed, but it cannot be asserted that a really complete coverage has been achieved.

CALCIUM CHLORIDE

Much work has been done in evaluating the possible effectiveness of calcium chloride as a soil stabilizing agent, and this literature has been aptly reviewed by F. L. Cuthbert. (1)*. The use of calcium chloride in stabilization was prompted by the establishment of the practice of using calcium chloride as a dust palliative for granular stabilized roads; it not only acted as a dust palliative but also tended to maintain in the road a moisture content which had a beneficial effect on the stability of the road itself. From then on much research was carried out to evaluate the various ways in which calcium chloride acted effectively in soil stabilization.

Most of what is said about the facilitation of compaction, retention of proper moisture content, and prevention of freezing by calcium chloride admixture, is quite obviously to be expected in view of simple theoretical considerations. But nothing can be said for calcium chloride in connection with soil solidification, as described in the introduction. In stabilization, the fundamental factors are "gradation, water content, and compaction" (1, p. 7) and the chemical stabilizing agent is used with the hope that such an admixture will help to maintain in the stabilized soil the specific optimum condition of gradation, water content, and compaction originally imparted. Hogentogler and Kelley state "stability depends upon the thickness of the adsorbed moisture films, and the principal aims of stabilization are to make the soil as dense as possible and to prevent the thickness of the moisture films from changing." (1, p. 8, taken from 3)

It is very likely that the phenomenon of base-exchange plays some part in soil stabilization by calcium chloride admixture. It is very reasonable to point out the good effect of such base-exchange in reducing the thickness of water-films around the clay particles, thus materially increasing the ease of compaction. It may be added that such base-exchange can only take place in so far as there are monovalent cations (Na, K) to be replaced, and therefore if calcium chloride does act by base-exchange, it can only be beneficial. Base-exchange of monovalent cations by calcium has one added advantage over most of the range of water contents, except at dried conditions. As reported by Winterkorn and Moorman (4, p. 415), calcium soil has the least amount of total volume change on application of loads, which indicates that the water films around the calcium-soil particles are compact; and the small increases of moisture content during reduction of pressure indicate small attraction

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* These numbers refer to a reference list on page 5.

for additional water. In soil stabilization, the characteristics of the soil when dry are ordinarily not considered, and so the fact that the bonding power of dry calcium-saturated clays is considerably lower than that of dry sodium-saturated clays is no deterrent. Most of the effectiveness of calcium chloride as a stabilizing agent is, in fact, dependent on its ability to prevent the soil from drying. Calcium chloride is deliquescent and hygroscopic; also calcium chloride solutions have lower vapour pressures than pure water at the same temperatures, which implies a decrease of speed of evaporation. Surface tension is also related to the rate of evaporation in that the higher the surface tension, the lower the rate of evaporation, and addition of calcium chloride to water causes an increase of surface tension. "There is some evidence to indicate that the increased surface tension of the calcium chloride solution may make the films around the clay particles stronger, and thus increase the cohesiveness or strength of the bonds between the sand grains." (1, p. 14, taken from 2) The author suggests that some academic research into the problem of comparisons of adsorbed water film thicknesses and bonding strengths of calcium and sodium-saturated clays (and other homoionic variations too) through the whole range of moisture contents from dry to completely saturated, may be helpful in clearing some of the concepts that are merely surmised on the basis of scattered evidence.

Further claims on the effectiveness of calcium chloride are that "aggregate loss is reduced: a reduction from 100% for an untreated road to 37% for a treated road is given for a controlled project." (1, p. 29) And finally, the fact that the addition of calcium chloride reduces the freezing point of water is given as an explanation for the reduction of frost heaving. Any salt dissolving in water will reduce the freezing point of the water.

The theory of soil stabilization by calcium chloride as above summarized will serve to explain the modicum of good results reported by various investigators. It is felt that the field has been fairly well exhausted by now, and the limitations of the procedure should be apparent. Any improvement made possible by a more accurate knowledge of the relations of exchanged ions to thickness and compactness of adsorbed water films and to bonding strengths, will not be revolutionary.

It must be noted that the above write-up considers only the sole application of calcium chloride. Calcium chloride has been successfully used in stabilization in combination with other reagents; for example, in soil-cements, or in the use of sodium-silicate. This will be discussed in connection with cement and sodium-silicate solidification, since the calcium chloride is the secondary factor in such processes.

Note. No attempt is made here to report on construction techniques, details of field experiments and so on. For information on these phases, the interested reader is referred to the bibliography which is submitted ~~under separate cover,~~ as Part III of the general report.

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   "Essentials of Soil Compaction," Proceedings, Highway Research Board, Vol. 16, 1936.

3. Hogentogler, C. A. and Kelley, J. A.
   "Role of Soil Binders and Aggregates in Soil Stabilization," Proceedings, American Road Builders Assoc., 1937.

4. Winterkorn, H. F. and Moorman, R. B. B.
   "A Study of Changes in Physical Properties of Putnam Soil Induced by Ionic Substitution," Highway Research Board Vol. 21, 1941.

SODIUM CHLORIDE

The use of sodium chloride in stabilization is similar in many respects to the use of calcium chloride. "Mechanically stabilized mixes with long gradings and binder-soil are essential for both, similar construction procedures are used, and the same general precautions as to usage should be taken." (1, p. 428)

Sodium chloride solutions have a lower vapour pressure than water, thus retarding the evaporation of moisture from the soil mixture. With prolonged evaporation, the sodium chloride solution reaches the saturation point at the surface and crystals of salt are deposited. It is claimed that this crystallization contributes to the strength of the stabilized mix. The addition of sodium chloride to a clay* tends to produce flocculation so that the soil mixtures become more dense under traffic, and consequently also relatively less permeable. When water falls upon such a road, surface salt dissolves and the brine seeps into the ground, considerably reducing the concentration of salt near the surface. The clay near the surface thus deflocculates and swells, plugging up the pores and preventing further percolation of water downward from the surface. "This action together with maintained compaction beneath the surface greatly retards the leaching of sodium chloride from the stabilized wearing course, thus preventing further deflocculation." (1, p. 429, taken from 2) As drying occurs the brine creeps to the surface by capillary action, and flocculation of clay and crystallization of salt again take place.

Note. Further consideration of theoretical concepts of the action of calcium chloride, sodium chloride and such simple salts in soil stabilization will be found in the section relating to the colloid chemistry of the clay minerals.

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* It must be noted that this is not true of all clays, especially not, for instance, of bentonite.

REFERENCE LIST

1. Belcher, D. J., McAlpin, G. W., and Woods, K. B. "Current Practices in Stabilization," Proceedings of the Purdue Conference on Soil Mechanics and Its Applications, September, 1940.

2. Report of Subcommittee on Treatment with Sodium Chloride, Highway Research Information Service, Highway Research Board, 1936.

CEMENT

General: Portland cement has found considerable application in soil stabilization and soil solidification. Under suitable conditions Portland cement grout may be injected into the undisturbed soil structure; whereas for the stabilization of surface soils dry cement is mixed with the soil at suitable moisture contents, and the mixture is compacted. In the latter application, the relative quantity of cement used determines whether the net result is a soil-cement or a cement-modified soil. In a cement-modified soil, the cement content is so low that all it can achieve is aggregation of fine particles into larger aggregates, thus effectively modifying the particle size gradation; in a soil-cement, actual soil solidification is effected.

Mechanism of Cement Stabilization: No information is to be found in literature on soil-cement roads regarding the chemical reaction between the soil and the cement. In fact, there is no basis for expecting any such chemical reaction, and the cement appears to have the same function in soil-cement mixtures as in aggregate-cement mixtures (concrete)--that of cementing the particles together to form a rigid mass. Portland cement is the binding agent, hardening by hydration. In soil-cements, the "aggregate" that the cement is to bind is the soil, and many properties of the soil determine whether or not the "aggregate" is suitable for cement solidification. Among these factors are particle size and grading, surface activity of colloids, and possible presence of organic acids and partially decayed organic matter which would be detrimental.

Since soil-cements do not use enough Portland cement to fill the voids, the cement merely "spot-welds" particles at their points of contact. (3, p. 59)* It is not the purpose of this review to analyze the conjectures and theories concerning the chemical reactions involved in the hydration of Portland cement and concerning the nature of the bond effected by cement. Suffice it to say that "a study of hundreds of soil-cement specimens during test and the performance of soil-cement field projects shows that the chemical changes involved in cement hydration are similar in soil-cement and concrete." (1, p. 842) However, several important soil characteristics determine the success or failure of soil-cement solidification, and these should be considered. M. D. Catton states that "such factors as grain size, gradation,

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* These numbers refer to a reference list on page 16.

silt and clay content, density, optimum moisture, water holding capacity, surface area, organic content, void-cement ratio, hydrogen ion concentration, etc., contribute to an analysis of soil and soil-cement relations, but they are so diverse and interrelated in character and influence that none of them have a constant, major, predominating influence." (1, p. 821) This statement is based on data from tests on 329 soils. The influence of each of the above factors individually may be qualitatively understood from theoretical considerations, but indeed none of these factors can be set down as clearly exerting a predominating influence, and eventually the only conclusive way of determining the feasibility of soil-cement solidification at particular projects is to test by a series of compression tests, wetting-and-drying tests, and freezing-and-thawing tests on molded specimens containing various cement contents. (It may be noted that the search for a predominating factor among all these diverse and interrelated factors cannot help but be fruitless: it is felt that much more significant results would be obtained by studying each factor individually with "synthetic soils" prepared so as to vary only one factor at a time.)

Gradation and Particle-Size: Available reports on soil-cement projects show a wide range in gradation of the soil. In general, granular material such as sands and gravels require less cement than do the more plastic soils. This is reasonable on the basis of surface area, all other factors remaining constant. On the other hand, the following statement by M. D. Catton was only to be expected: "However, as the data show, soils may have widely different surface area and yet respond to cement in a very similar manner. While surface area is recognized as a contributing factor, it cannot be used to predict cement requirements." (1, p. 849) Besides, the difficulty of determining the actual in-situ surface areas must be mentioned. The hydrometer test for determining particle size is open to serious objections in view of the fact that some clays would subdivide into extremely fine particles on being suspended in water. It must be recognized that the hydrometer test is only retained because there is no easy substitute.

Atterberg Limits and Density and Strength Relations: That Civil Engineers would have attempted to find relations between the Atterberg Limits and the feasibility of soil-cement solidification was to be expected. But no less was it to be expected that no simple relations would be found; and it is beginning to be realized that the Atterberg Limits themselves are too arbitrary, although indirectly related to more fundamental properties such as colloidal clay content, exchange capacity, and base-saturation. M. D. Catton is thus led to make the statement, as a conclusion from many tests, "it can suffice to say that the liquid limits, plasticity index, or surface area cannot be used as criteria for control of soil-cement mixtures." (1, p. 849) And yet, the fact that no simple consistent relation between these Atterberg Limits and the feasibility of cement treatment is apparent should not lead us to the false assumption that the influence of such factors is small. The Atterberg Limits are controlled by certain fundamental properties which also influence cement treatment; perhaps an investigation of more basic character would lead to more edifying relations. For the present, only general empirical statements can be made, as for example, the statement made by H. F. Winterkorn: "The soil requiring the lowest amount of cement for stabilization is one which possesses a small or negative difference between the optimum moisture content for compaction and the shrinkage limit, and which can be compacted with cement to give a system of great density and consequently low permeability"; (9, p. 401) or Catton's statement, "The data show that water-holding capacity, as reflected in the physical test constants, gives a general indication of cement requirements, which needs increasing with water-holding capacity." (1, p. 853) Whereas it is virtually impossible to analyze the former statement in the light of theoretical considerations, the latter should be fairly well deducible in view of the relation of water-holding capacity to surface area, colloidal content and reactivity, and such fundamental factors. Other information on the same subject is given by E. J. Sampson (6, p. 557), where, with regard to the effect of Portland Cement on raw soils, the statement is made, "as the curing time increases 1) the liquid limit remains practically constant 2) the plasticity limit increases 3) the plasticity index decreases appreciably 4) the shrinkage limit increases 5) the shrinkage ratio increases 6) the centrifuge moisture equivalent decreases 7) the field moisture equivalent increases 8) the quantity of coarse sand increases 9) the quantity of fine sand decreases 10) the percentage passing #220 sieve decreases 11) the silt content decreases 12) the clay and colloids content remain practically constant." And so on, a wealth of such empirical information is available; but correlation of all such data on the basis of fundamental concepts would be a very involved study. Such a study cannot possibly be attempted here. It is suggested that the institutions interested in conducting research on soil-cement tackle the problem more from a fundamental point of view, if necessary using synthesized soils with properly controlled variations of individual factors. It is felt that only such academic research will be beneficial in the long run, in further developing the judicial use of soil-cement solidification.

Short of detailing the theory that, as above mentioned, is still in the offing, the best that this review can attempt to do is to condense the welter of scattered information that might help in the development of such a theory. Any theory that is developed will have to satisfy such data.

The following general conclusions are drawn by J. D. Watson (6, p. 493): "1) The initial characteristics of a soil have more effect upon the compressive strength of a given soil-cement mixture than any other factor. 2) Increasing the percentage of cement in a given soil from 5 to 11 produces a greater increase in compressive strength than do the factors of varying density and varying moisture content. 3) The densest mixture of soil and cement will generally develop the highest compressive strength for a given soil and percentage of cement. 4) Because of the wide difference in the amount of water which is necessary to bring about maximum density, the water content ratio is not a suitable control for soil-cement mixtures. 5) As the cement content is increased from 5 to 15 per cent, some soils gain in compressive strength at a more rapid rate than the rate of cement increase. Within this same range other soils do not gain in strength as rapidly as the cement is increased. 6) Cycles of wetting and drying produced an increase in the compressive strength of mixtures of sandy loam and of some clay loam mixtures. 7) Cycles of freezing and thawing generally produced some decrease in the compressive strength of all cylinders."

M. D. Catton (1, p. 543) compares compressive strengths with maximum density, optimum moisture, cement content for "adequate hardness", hydrogen ion concentration, and organic content, as follows:

1) "There is no criterion for control on a density-strength relation basis.

2) "A pattern of decreases in strength with increases in optimum moisture is indicated.

3) "As the cement content for satisfactory hardness increases, the compressive strength decreases.

4) "The pH value of the soil is not a direct primary factor influencing the compressive strengths of soil-cement mixtures. It is clearly shown that the same strength can be obtained with soils having a wide variation in pH value from high acid to high alkaline.

5) "Data show that there is a definite trend for compressive strengths to decrease as the organic content increases."

Surface Chemical Factors: In 1940, after five years of research dealing with the physical properties of soil and soil-cement mixtures, M. D. Catton made the following statement, "All the test data also indicate that some factor is present in soil which does have a prevailing influence on the ability of cement to harden the compacted soil-cement. The fact that compressive strengths vary for soils having similar density, similar strengths, similar water-holding capacity, and other similarities gives substantial support to the hypothesis that there is some such factor, other than physical relations, which plays an important role in determining the influence of soil in compacted soil-cement relations. Therefore, the chemical composition of the soil and, possibly, the nature of adsorbed ions are factors which must be tested, studied and evaluated." (1, p. 854) H. F. Winterkorn's work (11) establishes that soil aggregate of soil-cement is capable of surface chemical activity (adsorption of cations) which seems to have a marked effect on the cement setting processes. As a result of a research project investigating the effect of surface adsorbed cations on the hardening effect of Portland cement in soil, H. F. Winterkorn arrives at the following conclusions, among others: "The results show: a) that the surface-chemical along with other physical factors influence the hardening of clay soils with Portland cement, b) that ionic treatment can improve the hardening action, c) that the water affinity and the accessibility of the internal surface of the soil cement system controls its behaviour in the wet-dry tests, d) that the permeability of the system and the amount of pore space filled with unadsorbed water determines its behaviour in freezing-and-thawing tests." (8, p. 385)

The pH of Soil: The definition of pH (hydrogen ion concentration) properly applies to aqueous solutions; in the case of two- or three-phase systems such as soils some question may be raised as to the meaning of the term "pH". This term as used in soils refers to the reading obtained using some electrode scheme on a commercial instrument, such as the "Beckman pH meter". This reading for a given soil is meaningless unless taken in situ, at known moisture content; (4) increased water content may cause a pH reading on the acid side to change to a reading on the basic side, and a destruction of the balance of in situ bacterial activity may seriously alter the pH reading. No mention will here be made of the methods of measuring pH and the precautions necessary; suffice it to say that such considerations are of very major importance if the results reported by various investigators are to be of any significance.

It appears that the pH meter measures only the hydrogen ion concentration of the unadsorbed soil water: i.e. any adsorbed hydrogen ions do not influence the pH reading. Nevertheless, these adsorbed hydrogen ions are just as effective as unadsorbed ions in the reduction of available calcium for hydration. So M. D. Catton's statement that "these tests and data show that a soil may be acid, neutral or alkaline and will respond equally well to cement, yet the test for pH by itself is not significant in indicating cement requirements," (1) should be expected. And it is not merely necessary to consider the soil water pH along with the number of adsorbed hydrogen ions in order to get a good indication of a soil's suitability for cement stabilization. H. F. Winterkorn states: "The Putnam clay has a relatively high base exchange capacity. The hydrogen Putnam soil, therefore, represents an acid material which is liable to take away from the Portland cement a considerable amount of calcium ions and thus reduce its cementing power. The fact that with low cement contents the Hydrogen-Putnam is by far the worst, while with high cement content it falls in the same group as the magnesium and calcium soils, indicates the justification of this point of view." (8 , p. 402) And further: "The bad showing at low cement contents of the hydrogen systems in the case of Hays, Hagerstown, and Putnam soils which all possess a relatively large base exchange capacity appears to be due to the same cause, namely the deprivation in calcium ions of the Portland cement. These ions are used up in the neutralization of the hydrogen soils." (8 , p. 408) These statements tend to indicate that the effect is indeed related to a pH effect, being specific for hydrogen ions. It seems much more likely, however, that the effect is one related partly to base-exchange, in which case, even a sodium saturated soil is capable of depriving the Portland cement of some of its calcium ions.

That acids are detrimental to Portland cement is known.

Effect of Organic Matter: M. D. Catton, on the basis of much experience, states that "when organic content (author's note: determined colorimetrically) exceeds 5000 p.p.m. the soils are acid." "It does not show that if the soil is acid it will have a high organic content." (1, p. 836) It thus obtains that high organic content would be detrimental through acidity. H. F. Winterkorn states: "The presence of soil organic matter appears to be undesirable, especially if it is of an acid nature." (8 , p. 414) There are many kinds of organic content that are inert. M. D. Catton (1, p. 838) mentions two such inert classes of organic matter. 1) undecomposed vegetation such as roots and twigs, and 2) insoluble carbon compounds, such as coal, lignite, etc. In a discussion of the detrimental effects of organic matter on certain stabilizing treatments, H. F. Winterkorn establishes a distinction between dry-land and wet-land organic matter. (5, p. 12)

The use of the colorimetric test rather than combustion tests for soil organic matter is a step in the right direction in trying to distinguish between the two kinds of organic matter. But there is no assurance that such a distinction is clearly brought out by the colorimetric test, and it is felt that this is in part responsible for the futility of hoping that the colorimetric test will infallibly disclose unfavorable cement reaction factors. (11) Of course, "high results in the colorimetric test may indicate that a detrimental cement factor is present." (1, p. 840) But then, "data indicate that for northern soils (podzols etc.) when the colorimetric tests show about 2000 p.p.m., or more, the contained organic material may likely influence the action of the cement, as shown by reduced compressive strength;" while on the other hand, "soils from the southeast and south (red and yellow soils, not from poorly drained sand areas) and from the far west may contain considerable organic matter (10,000 to 30,000 p.p.m.) and still react normally with low cement contents." (10, p. 52)

One further reason why it has been difficult to study the effect of organic matter is that in studies of natural soils this effect cannot be isolated. M. D. Catton's attempt to find a relation between organic content and the Atterberg Limits, compressive strength, and cement content required for adequate hardness, draws the following conclusions: a) "The comparison of organic content and physical test constants brings out the fact that the sands and silts in this study may have high organic content with the clays generally having low organic content." b) "There is a definite trend for compressive strengths to decrease as the organic content increases." (1, p. 839) But, of course, it was to be expected that it would be found that soils having wide ranges in organic contents may require the same cement content for adequate hardness.

Various admixtures have been used to combat the detrimental effects of organic matter (organic acids). In the case of sandy soils with a deficiency of fines, addition of clay may improve conditions, since the clay adsorbs organic matter preventing its reaction with the Portland cement. (2, p. 498) Calcium hydroxide, calcium oxide, calcium chloride, and calcium carbonate have also been used. The effective use of these chemicals for combatting the detrimental effects of organic acids and hydrogen-soils is to be understood from a consideration of the two likely reactions taking place; namely, neutralization of the acids and base-exchange of the clay. M. D. Catton and E. J. Felt state that the action of calcium chloride is that it "inactivates the organic matter;" but this is not clearly understood. Calcium chloride is very effective in improving the cement reaction with poorly reacting sandy soils, but has a minor effect on normally reacting soils. The beneficial effect of the calcium chloride appears to be permanent. Catton and Felt also state that "in some instances the quantity of cement saved was 50 per cent or more if the quantity of calcium chloride added to poorly reacting soils was of the order of 0.6 to 1.0 per cent by weight of soils." (2, p. 527) Note, however, that such admixtures have other effects on the Portland cement, such as increasing the rate of hydration of the cement; these will be mentioned below.

Density and Moisture Content Relations: H. F. Winterkorn and many other investigators give much information on this subject, which has been omitted from consideration in this report. (8) The interested reader is referred to some of the publications listed in the bibliography, in Part III of the general report.

Winterkorn finds that the density of a soil-cement system almost determines the compressive strength. Soils possessing low optimum moisture contents can usually be compacted to high densities. Increasing the density at constant moisture content decreases the accessibility of the internal soil surface and the pore space available for freezing water, which is an improvement. Increasing the moisture content at constant density exerts a general beneficial effect: the reason for this may be an increased satisfaction of the water-binding ability of both soil and cement.

Similarly, M. D. Catton finds that the optimum moisture for maximum density, maximum compressive strength, and maximum weathering resistance (wet-dry, freeze-thaw) are about the same, and suggests that it is best to use a moisture content slightly higher than the optimum for density and strength. (1, p. 526) W. S. Housel claims that "Throughout the investigation it became increasingly apparent that the behaviour of the mixture must be associated in some way with voids, and that the efficiency of cement stabilization depends in some way on a relation between voids and cement," and establishes that "a cement-voids ratio of 15 per cent may produce a mixture as durable as present requirements indicate is essential." (3, p. 58)

These scattered comments will serve to point out that the considerations of mechanical stabilization of soils, compaction, etc., are important. They are omitted from consideration in this report, but that does not detract from their importance.

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6. Sampson, E. J. and Henderson, H. G.
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7. Watson, J. D.
"The Unconfined Compressive Strength of Soil-Cement Mixtures," Proc., Highway Research Board, Vol. 21, 1941.

8. Winterkorn, H. F., Gibbs, H. J., and Fehrman, R. G.
"Surface Chemical Factors of Importance in the Hardening of Soils by Means of Portland Cement," Proc., Highway Research Board, Vol. 23, December, 1942.

9. "Method of Chemical Determination of Cement Content of Soil-Cement Mixtures," Portland Cement Association, Chicago, Illinois, January, 1942.

10. Soil-Cement Mixtures Laboratory Handbook, Portland Cement Association, 1942.

11. "A Critical Laboratory Review of Methods of Determining Organic Matter and Carbonates in Soils," U.S. Department of Agriculture, Technical Bulletin No. 317, June, 1932.

Effects of Various Admixtures on Cement: Although not all of the following reports refer to soil stabilization, it can well be seen that the information made available in such reports may be used to modify cement for specific purposes in soil solidification.

1) "The Effect of Calcium Chloride Admixture with Portland Cement," J. R. Shank, Ohio State University Engineering Experiment Station Report.

The following results are brought out: 1) In hot, dry places large proportions of calcium chloride may be used without serious reduction of durability and strength. 2) Large proportions of calcium chloride should not be used in construction exposed to weather, freezing and thawing.

2) "The Use of Calcium Chloride as an Accelerator for Portland Cement," H.T.S. Swallow, Civil Engineering, London, Vol. 33, No. 387, p. 343-7, 1938.

3) "Early Strength Concrete: The Use of Calcium Chloride in Concreting," Calcium Chloride Association Bulletin #28.

Methods of using calcium chloride in concrete and also the advantages of it such as faster setting, increased workability, and prevention of damage from cold weather are described.

4) "Contributions to the Study of Soil Stabilization by Means of Cement," Hummelsberger, Betonstrasse, Vol. 14, No. 10, Vol. 201, No. 11, p. 221, 1939.

A series of experiments with sand-clay mixtures indicated that with cement the most promising range of sand-clay is 70:30 to 50:50. Peat and humus were found to be injurious to cement. Experiments were made to improve cement stabilization by addition of calcium chloride, sulphite lye, blast-furnace slag, or tar: mixtures were strong but insufficiently resistant to water.

5) "More Durable Concrete with Treated Cement," M. A. Swayze, Engineering News-Record, Vol. 126, No. 25, p. 946, 1941; Journal of American Concrete Institute, Vol. 13, No. 1, p. 87, 1941.

Resistance to frost action was increased by adding small quantities of mineral oil, animal or vegetable fats or oils, natural resins. Frost resistance was improved, workability and plasticity were increased, and bleeding was reduced by the resins and fats (not appreciably by the mineral oils). The optimum quantities without reducing the compressive strength too much are: mineral oil 0.04 to 0.06 per cent; animal fats or oils, 0.01 to 0.03 per cent; Vinsol resin 0.02 to 0.03 per cent. Vinsol resin was the best reagent.

6) "Mixtures of High Alumina Cement and Slag Cement for Injections," Bardout, Age du Ciment, Jan. 3-10, 1938; Sci. and Industr., Vol. 22, No. 62, p. 21, 1938; Building Science Abstracts, Vol. 11, No. 2300, 1938.
Injections were made in soil with a large content of water containing gypsum. A mortar of low cost with a very rapid set was required. Investigations were made to determine the most suitable proportions of slag cement and high alumina cement.

There are probably cases where the use of high alumina cement for soil solidification will be required.

7) H. Barron (India Rubber Journal, Vol. 91, pp. 167-170, 199-203, 1936) discusses the nature and properties of various hydraulic cements and concrete: a review of modern practice in the use of cement and latex mixtures in the production of road and surfacings follows. (Vide page 78)

8) J. W. Kushing (Roads and Streets, Vol. 84, No. 12, pp. 23-30, 1931) makes some general observations on concrete scaling; organic admixtures showed satisfactory resistance.

9) "The Function of Entrained Air in Concrete," Henry L. Kennedy, Journal of American Concrete Institute, Vol. 14, No. 6, June, 1943.
Cement dispersion is a recent improvement of cement in concrete. Dispersion of the cement produces three important effects, it is claimed: a) The water which had been trapped within the particle clumps is released to become a part of the mixing or placing water. b) The surface area in contact with the water is greatly increased since the particles are no longer in contact with each other. c) A certain amount of additional air is entrained.

10) "Pozzolith-Cement Dispersion and the Water-Cement Ratio Law," Pamphlet, The Master Builders Company, Cleveland, Ohio.
Plasticity or workability of concrete can be markedly improved by the use of two general classes of additions: "a) Catalyst-dispersing agents which function by lubricating the cement without entraining appreciable air, thus increasing the fluidity of the cement paste matrix in concrete. b) Many air entraining agents, such as some wetting agents, resins, etc., introducing well distributed air bubbles which appear to act as ball bearings and decrease the particle interference of the concrete aggregates." Entrained air improves resistance to freezing and thawing. One of many different air entraining agents including fatty acids, wetting agents, (such as sulfated alcohols and sulfonated hydrocarbons) oils, and resins can be used. Gas generating agents such as aluminum powder

and hydrogen peroxide have been used with good result. Air-entrainment beyond a low optimum decreases the compressive strength. Dewey and Almy Chemical Company claim that their Darex air-entraining agent combats this loss of strength by the use of a catalyst that makes available more of the inherent strength of the cement.

The use of such modifications of cement in soil-cement stabilization may be worth investigating. The dispersing effect would probably be advantageous; the air-entrainment may not, since soil-cement could probably be improved by decrease of air-voids. The use of gas generating agents in calculated quantities offers an interesting possibility; H. F. Winterkorn used foaming agents for the purpose of concentrating the cementing resins on the points of contact of the soil particles. ("A Laboratory Study of the Soil Stabilizing Effectiveness of Artificial Resins with Special Emphasis on the Aniline-Furfural Resins," Civil Aeronautics Administration, Washington, D. C., Note No. 43, p. 7, January, 1947.)

BITUMENS

Bituminous materials have been used extensively in stabilizing improperly graded soils. The function of bitumen in stabilization is mostly that of producing in the soil materials a high degree of immunity to the deleterious effects of water, as is recognized by most investigators. B. I. Scoggin says that "the only excuse for the use of bituminous material for soil stabilization is to make it resistant to the effects of moisture." (19, p. 501) However, the more heavy grades of bituminous materials do impart some degree of binding action to the soil, especially as used in stabilization of sands.

V. A. Endersby (6, p. 442) states that "There are two theories regarding the action of oil in waterproofing soil. One is the 'plug' theory which holds that the capillaries are simply plugged with bodies of oil, preventing the water from either entering or leaving. The other is the 'intimate mix' theory, under which the individual particles are supposed to be coated with oil. Neither can be considered as covering the whole ground, though the 'plug' theory, on a simple statistic basis, must be nearer the truth. The mineral surface in a clay is so enormous that no amount of oil ordinarily used can be expected to coat it completely.

"Moreover, if such large amounts of oil are used, the soil becomes lubricated by the oil and loses much stability on that account long before a perfect waterproofing coat is achieved. Because of the high viscosity of the oil, an excess of oil also prevents compaction. Thus stabilization does not improve in ratio with the amount of oil used, but begins to decline in quality beyond a certain amount of oil.

On the other hand, the oil plugs exist largely in the form of films partly spread over the particles. This is exemplified by the fact that if the oil is treated in such a manner as to promote spreading, the efficiency of the stabilization is increased."

C. L. McKesson finds, however, that careful laboratory study of the phenomena involved in bituminous stabilization "disclosed that the minute asphalt particles dispersed in the emulsion were intermingled with the soil colloids during the mixing process, and that when the water evaporated, these particles were pulled out into thin asphaltic films which, by coating the soil grain surfaces, caused them to become water repellent. In other words, soil colloids which had a cementing value due to the presence of an adsorbed film of water were caused to retain, instead, an absorbed coating of asphalt which resisted water infiltration. When attempts were made to remove the asphalt coating from the soil grains, it was found that the asphalt, under the tremendous force of adsorption, had become almost a part of the soil itself, to such an extent that only a small portion of the asphalt could be recovered with the usual solvents." (13, p. 283)

These findings of McKesson's need not be considered contrary to Endersby's concepts. They do not seem to be as general as Endersby's concepts. Endersby acknowledges that "the action of the oil is not a simple plugging of capillaries. A definite soil system exists, which changes its nature with the degree and method of mixing; and so far as waterproofing is concerned, the process passes through an optimum phase during the progression of mixing." (6, p. 444) The stages or phases are listed approximately as follows:

"1) The oil is distributed through the soil in large masses having little waterproofing value.

2) These masses are broken down until a substantial 'plugging' action is evident.

3) The oil is distributed over aggregations or 'cells' of soil particles.

4) At first these cells are too large, and the entrance of water into individual cells imperfectly waterproofed breaks down the soil as a whole.

5) An optimum condition is reached where the cells are small enough so that failure of individual scattered members is not serious.

6) The cells become too small, hence imperfectly waterproofed, because the oil is distributed too thinly.

7) A condition approaching 'intimate mixing' is reached. In this region some stabilizations continue to improve; others break down completely." "The reasons for the difference are quite complex." (6, p. 444) It may be seen that careful control of the mixing phases is vital to the best results.

Bituminous material used as admixtures in stabilized road construction may be divided into two groups, asphalts and tars. The asphalts are further divided into cut-backs, road oils, and emulsion. Belcher, McAlpin and Woods in their paper on "Current Practices in Stabilization," (2, p. 432) give a table of quality tests for bituminous materials.

	Tar		Asphalt
	AASHO	Tent. ASTM	Tent. ASTM
Ductility			D 113-35
Sampling	T-40-35	D 140	D 88-33
Specific Visc.	T-54-35		D 139-27
Float	T-50-35	D 139	
Specific Gr.	T-43-35	D 70	
Total Bitumen	T-44-35	D 4	
Water	T-55-35	D 95	D 96-35
Distillation	T-55-35	D 20	D 402-36
Softening Pt.	T-53-35	D 36	
Penetration			D 5-25
Flash pt.			D 92-33
Solubility			D 4-27

Asphalts: Asphaltic bitumen has been defined by the Fifth International Road Congress' Committee on Standardization as "Natural or naturally occurring bitumen or bitumen prepared from natural hydrocarbons by distillation or oxidation or cracking; solid or viscous, containing a low percentage of volatile products; possessing characteristic agglomerating properties, and substantially soluble in carbon disulphide." (2, p. 433) The asphalt must be converted to liquid form for easier application, and this is done either by heating or by dissolving in appropriate liquids or by emulsifying.

The asphalts dissolved in solvents such as benzene, naphtha, gasoline, turpentine, or oily liquids of sufficiently high surface tension form the common class of cut-back asphalts. These are furnished possessing the viscosities desired. Common designations are Rapid Curing (RC), an asphalt cement dissolved with gasoline, and Medium Curing (MC), using kerosene as a solvent, and Residuals or Slow Curing (SC), liquid asphalts consisting of asphalt and oils of low volatility.

Emulsion Stabilization: Emulsification of asphalt has been much used. "Stabilization by this process consists of mixing emulsified asphalt with earth in a proportion which will cause the binder, or clay, portion of the soil to lose its affinity for water, without causing it to lose its natural binding quality and become thermoplastic." (14, p. 856) The asphalt is dispersed throughout the medium in minute globules with diameters of the order of 1×10^{-5} cm. Oil-in-water emulsions are the more common, but water-in-oil emulsions are also known. The preparation of the emulsion requires the use of small amounts (usually about 1%) of a dispersing or emulsifying agent. Emulsions contain between 30 and 80 per cent water in extreme cases, usually about 50 per cent. The emulsifying agents used must render the emulsion particularly stable as a precaution towards the great variations of soil conditions encountered on single projects. Both alkaline, acid, and neutral emulsifying agents have been used; common alkaline agents are alkali soaps of fatty acids, alkalis, alkali silicates, organic bases, oxy-acids, proteins, and resins. The emulsion, if properly manufactured and correctly applied, should "break" at the proper time leaving a layer of asphalt on the mineral particles. In stabilization work slow breaking emulsions may be necessary because of the slow mixing operations.

The emulsion must also have the property of allowing unrestricted loss of moisture from the mixture after it is laid, so as to decrease setting time. Probably the most important requirement for successful asphalt-emulsion stabilization is that "the mixture must be dried to the lowest water content possible, in order to convert the spheres of asphalt into protective films on the soil grains." (14, p. 857)

The amount of asphalt required by this process is critical. Too small an amount will not render the soil sufficiently water resistant, and too great an amount, still much below the usual binding quantities, lubricates the soil so that it loses natural stability. Special tests have been developed to determine this critical value; among these, the most commonly used are the capillary absorption and the so-called "stability test."

Construction items such as proper mixing, adequate compaction, thorough drying, and proper surface protection are very important. B. I. Scoggin states that there is no doubt that high density is commendable, but maximum dehydration is a more important factor effecting durability of soil stabilized by the use of emulsified asphalt. (20, p. 498) There is a tendency towards the use of wet mixes to ease the mixing operation and render it most efficient, but it should be borne in mind that the increased drying time may be a serious drawback. L. Muir, W. Hughes, and G. Browning state that when emulsions are used the water content of the mix should be as near the plastic limit as possible at the time of mixing, and at the optimum water content during compaction. They also report that general practices with emulsified asphalt are substantially the same throughout the country, (17, p. 308) and list the following general rules. "1) The stack must be kept moist to about the plastic limit until mixing is complete. 2) Spreading, rolling, and dragging must be done when the material is at the proper consistency, which is about the optimum moisture content." "It is important that the emulsified asphalt contain no appreciable amount of soap or other soluble emulsifying agent, because experiments have shown that soaps in excessive amounts are very detrimental to the life of the surface."

Emulsion stabilization has unquestionable value since, because of the water content, it disperses through aggregate better than other types of asphaltic materials. However, emulsified asphalt must have certain characteristics for best results. "It must be of a mixing type, that is, it must thoroughly coat all soil particles; it must be miscible with water in all proportions; it must be capable of mixing with clay or the finest rock dust without balling; it must be able to lose its water vehicle rapidly after mixing; it must leave the remaining asphalt, after dehydration, uniformly dispersed as a light film upon all soil particles." (17, p. 308)

The versatility of emulsified asphalt for use in soil stabilization is such that usually it is merely a case of working out the best material for particular conditions at any project. Almost every property of the material may be modified by proper admixture, to suit given conditions. The only particular objection to it is one of economy.

<u>Use of SC, MC, and RC Oils</u>: These oils vary as to viscosity, curing properties, and chemical nature, and so afford wide selection for conditions at different projects. Only a few general principles are available to guide such selection, and laboratory testing should always be undertaken with a view to checking any choice. Very high viscosity is undesirable as making the oil too difficult to mix with the soil. Increasing the mixing temperature in order to lower the viscosity of the cut-back should not be resorted to, because the net effect appears to be negative in character. (9, p. 448) V. A. Endersby recommends that Grade 2 (e.g. MC2*) be the highest grade used. "With regard to curing properties, the question is probably more open. Rapid-curing oils may give trouble during any prolonged process of mixing and compacting. Slow-curing oils may not develop sufficient film stiffness. On the whole, the preference seems to be for medium-curing oils." "Oils differ very much in chemical nature. It is desirable to use oils which have a high affinity for mineral surfaces, and this affinity can be improved by chemical treatment. Cracked oils have it by nature, but are known to have undesirable traits in some other applications, and their use in soil stabilization has been insufficiently investigated." "Improvement of the oil in adhesion can be effected either by decreasing

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* These grades refer to viscosities, e.g.
No. 2 Grades (100-200 Furol viscosity at 140°F.)
No. 4 Grades (125-250 Furol viscosity at 180°F.)

the surface tension or by increasing the affinity for mineral, or both." "Oils can also be improved by adding agents which stiffen the film upon curing." (6, p. 448) Some of these additives will be considered later.

The correlation of the composition of asphalts of the slow-curing type with their physical properties has been made by J. Zapata. (28, p. 160) A few of the results he obtained are listed in the following table.

Physical Property	Change with Composition	Correlation with other Properties
1. Surface tension	Increase with increase of resin or asphaltenes	Stripping resistance increases with specific gravity
2. Viscosity	Increase with increase of resin or asphaltenes	Stripping resistance increases with increase in viscosity
3. Accelerated weathering	Varies with asphaltenes and type of asphalt	Connected with evaporation

The proportions of soil, asphalt and water which are to be used are selected by laboratory tests corresponding to maxima of curves of Hubbard stability load vs. percentage of asphalt cut-back, or optimum conditions of low water absorption or low volumetric swell. "In general, the major design is based on results obtained with uncured soil--water--cut-back mixtures which have been exposed to the direct effects of water." (18, p. 299)

Miller and Klinger established that the "dry-mix" method of construction is most suitable for soil stabilization. (16, p. 132) "Relatively low moisture content in the soil is still believed to be desirable since field manipulation is decreased, immediate compaction is possible, failures resulting from unexpected rainfalls are reduced and the hazard of visually estimating the time when a 'wet-mix' can be compacted is eliminated." (18, p. 301) "It has been found that when the proper combination of asphalt cut-back and water is incorporated with the soil so as to obtain maximum stability, the necessary compaction is also obtained. This need not be the same as maximum compaction. We have found no relation between strength and density. We do know that the strength is considerably less at maximum density than at maximum stability." (18, p. 301)

For slow-curing and medium-curing oils, the water content should be at about optimum for both mixing and compacting. (17, p. 6) Endersby considers Benson's "fluff point"* a simple and adequate guide to proper water content for mixing with oil, in order to give the water time to infiltrate the soil cells and break them down to a satisfactory fineness in mixing. (3)

Holmes and others (9) undertook a detailed study of dry soil densities and strengths of compacted mixes using various liquids and oils covering a wide range of viscosities. Their results will not be discussed in detail. They state that "some of the liquids investigated are obviously impractical for field use but the high strengths obtained, although associated with relatively low dry soil densities, warrant further study of the use of the non-asphaltic petroleum oils with soils." Maximum dry soil densities are no longer considered all-important. "In a survey on the properties of soil-water-asphalt mixtures it appears that maximum dry soil densities, maximum strengths after water absorption, minimum water absorption and volumetric swell do not occur at identical compositions of the briquettes; but for any one series of briquettes made with constant amounts of water and increasing amounts of cut-back in the order of the property given."

They further discuss the use of the exudation value in the design of stabilized soil. (9, p. 422) "The exudation value is that quantity of liquid which a soil can contain without being squeezed out under consolidation or without producing a plastic mixture: in addition to being related to the specific properties of the soil, the exudation is further dependent upon the liquid added, such as water, asphalt or their mixtures, the consolidating load applied and whether the loading is applied continuously or intermittently." This will not be discussed further. The authors claim that "for preparing soil-asphalt mixtures, satisfactory results will be obtained when the ratio of the soil fraction passing a No. 10 sieve is greater than 1.75 to 2.0. For soils showing a smaller ratio, special studies should be made."

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* Benson uses a "fluff point" based on the fact that as water is added, the soil reaches and passes through a condition in which it becomes loose and "fluffy" with a moist appearance. When the condition is passed, it becomes cohesive and "muddy." Benson mixes at the upper fluff point.

The same article also reports results of various other investigations. The addition of wetting agents to increase the maximum dry soil density was tried with the use of an effective wetting agent of the sodium tetraisobutylphenol sulfonate type, but without effect. Asphalt stabilization of chemically treated soils was also studied. The complete data indicate that lime pretreatment of the soil gives by far the best results; potassium permanganate has moderate beneficial effect; the other chemicals tried appear to be without practical interest. Heat treating soils preliminary to bituminous stabilization was studied; the results indicated that heat treating refractory soils can improve their properties from the standpoint of bituminous stabilization.

Use of Tar in Soil Stabilization: "Tar is defined as a bituminous product which yields pitch when partially evaporated or fractionally distilled, and is produced by the destructive distillation of organic materials such as coal, petroleum, wood, lignite, and peat." (2, p. 435) Specifications define grades of tar from RT-1 to RT-12 and include two classes of cold mix material. The higher the number in the designation, the heavier the tar. For stabilization work, the first six grades, from RT-1 to RT-6, have been used successfully. Grades above RT-6 have proved too heavy to mix properly with the soil. The selection of grade is based on the soil and the climatic conditions. Sandy materials mix readily with the heavier grades, especially under high average temperatures; whereas the light grades are needed for the clays and fine grained soils.

G. E. Martin states, "A relative improvement in the supporting power of natural soils under load is obtained by the use of tar products as admixtures with the soil. The soil is also made water-resistant. As a general rule, the tar acts as a waterproofing agent, and the natural binder in the soil serves as the cementing medium. In the stabilization of very sandy soils, the tar acts as a binder." (15, p. 275)

Generally speaking, the heaviest grade of tar which can be satisfactorily handled should be used. Actual determination of grade and amount of tar to be used is based on laboratory tests. Commonly, "the amount of tar to be used is determined in the laboratory on the basis of material passing the No. 10 sieve and including any sand or other aggregate which is to be added to the project. This is the tar needed to make a satisfactory soil mortar." (15, p. 275) For efficient compaction, optimum water content relations ought to be observed; half the tar added to the soil may commonly be considered as moisture in obtaining the optimum moisture content during construction. Grading is not of major importance in tar stabilization.

The literature on bituminous soil stabilization would be scant and one-sided (dealing mostly with design and construction) unless supplemented by the literature which mostly relates to improvements of bitumens for road surfacing. Some of the literature that will be considered below will, therefore, be seen to have no more than indirect reference to soil stabilization. It is mentioned, however, in order to give an idea of the type of information available; it is not attempted to make this treatment in any way complete.

Much work has been done on the study of the problem of the adhesion of bituminous materials to minerals. Winterkorn and Eckert (26, p. 204) investigated the physico-chemical factors of importance in bituminous soil stabilization using natural and homoionic varieties of various soils.* They determined that cations of high valency are more desirable than those of low valency, and if the valency is the same, those ions with large radii and consequent small water affinity are more desirable. "With most soils, excepting perhaps the lateritic ones, the valence effect takes precedence over the size effect." Small silica-sesquioxide ratios of the clay particles are beneficial. Further points that are noted are: (1) hydrophobic organic films protecting the mineral constituents improved results; (2) hydrophilic organic matter (which develops in moist conditions in rather tight and fat soils) is a liability. It was noticed that almost in all cases the higher the asphaltene content in the stabilized soil, the better was the latter protected against water; it is stated, however, that other possible influences, such as total bitumen content and chemical character of the bitumens should not be overlooked.

With respect to the surface chemical aspects of bituminous stabilization, H. F. Winterkorn makes the following statements: "The physico-chemical character of a certain surface is a function of the chemical composition and of the geometrical structure of the surface layer." "The attraction of water by the surface of the soil constituents is primarily due to electrical charges on this surface and also to the dipole character of water molecules." (25) A certain amount of moisture must be present in the soil in order to ensure successful bituminous stabilization. "When the heated oil comes in contact with the water film on the soil particles, its polar constituents orient themselves in a way to bring their active heads in contact with the aqueous phase. The elevated temperature of the oil increases the speed of migration and orientation." Thus, on evaporation of the free water present, "the active parts of the constituents of the

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* The effects of cations, anions, and various acids, bases, and salts on physical soil properties were also investigated by Holmes and collaborators, (9) and Winterkorn and Moorman. (27)

bitumens have a chance to react physically or chemically with the mineral surface."

"(a) If the mineral surface possesses a preferential affinity for the polar constituents of the bitumen, mixing of the mineral aggregate and the bitumen at elevated temperatures will be adequate."

"(b) If the affinity of the mineral surface for the bitumen is very small, a changing of its surface character by exchange adsorption with more suitable ions, or by precoating with molecules with dual character like those of soaps, naphthenic acids," etc., is advisable.

"(c) If the amount of surface involved or the character of the surface is such as to render impossible the adequate removal of the adsorbed film by heating, then use should be made of the orienting influence of water on the character of the bituminous interface, either by specifying a certain moisture content of the mineral matter or by the use of emulsions." "The beneficial action of emulsions is not so much due to their decreased viscosity, but more to the fact that the surfaces of the bituminous globules contain the active particles in an orientation which is most favorable to the desired reaction with the mineral surface."

This beneficial action of soap-like molecules in orienting the active particles in the bitumen is fully discussed in another article by H. F. Winterkorn, (23). The article further reports results on investigations into the use of sodium-Ivory and potassium soaps. It was found that tensile strength and water resistance of samples was greater in systems of oil-soap solution-soil than in those of oil-water-soil, and the system oil-dry soil gave the poorest results. In all cases, where soils had a relatively low content of organic matter, soap showed good effects. Sodium soap was better with low colloid contents of the soil, while potassium soap was better with high colloid contents. With increasing organic matter, the soap influence became erratic, probably due to dispersing and dissolving effects of alkali ions on the organic matter. Coagulation of this organic colloidal material with calcium chloride and subsequent treatment with oil and soap solution resulted in non-shrinking, water-resistant systems. A small addition of copper sulfate ($CuSO_4$) to these systems proved especially beneficial.

$NaOOC$------------$CH_2-CH_2-CH_2$---CH_2

$NaOOC$	$CH_2-CH_2-CH_2-CH_2$
Inorganic Character; Affinity to water	Organic Character Affinity to oil

R. Grader studied the adhesivity of bituminous binders and states that the causes of adhesivity of bituminous binders to stone should not be sought in mechanical or physical effects at the surfaces of contact. He assumes to be influenced by polar substances, and shows by means of examples the effect of the length of the C-chain in the molecule on adsorption, and the special effect of the saturated carboxylic acids. (8) W. Becker (1) furthered this study by investigating the additions of small quantities of fatty acids, oils, waxes, or organic salts of heavy metals. His results showed that aromatic or unsaturated aliphatic fatty acids had no effect, whereas saturated aliphatic acids caused a distinct improvement which was more pronounced as the length of the C-chain increased; dicarboxylic acids were much more effective than monocarboxylic acids, when atomic numbers were the same; carboxyl, hydroxyl, and amino groups had similar effects. The results were not related to the chemical composition of the stone, and, therefore, cannot be dependent on chemical activity. Adsorption is indicated, and since adsorption increases as the molecular weight increases, within a single group, the influence of the C-chain is explained. Thus it is claimed that in untreated binders the adhesivity depends upon the adsorption of substances of high molecular weight. These are asphaltenes, in the case of bitumens, and "free carbon" or material insoluble in benzene in the case of tars.

The problem of adhesion between minerals and bitumens was also studied by H. F. Winterkorn. (24) Adhesion is increased with an increasing amount of active components of the bitumen which are preferentially adsorbed by the mineral; and the formation of water and oil insoluble compounds with constituents of the mineral is beneficial. These active components of the bitumen may be very stable (acids in natural asphalts), or very unstable if produced by excessive heating. "Compounds showing special affinity for the hydrophilic, quartzlike, type of aggregate are usually of the latter type. While exhibiting desirable adhesive properties, they generally possess an undesirable weathering susceptibility." It is most desirable to use aggregate which has no affinity for water in connection with asphaltic material of good weathering resistance. "The main problem in the field of adhesiveness is, then, to change the surface properties of hydrophilic mineral which is not susceptible to improvement by base-exchange or which does not possess the advantages of a porous structure for lodging of asphaltic plugs or filling by polyvalent metal salts."

"Hydrophilic mineral is normally covered by a thin moisture film, even when apparently dry, and hence a three-phase system (solid mineral-moisture film-bituminous film) is involved. A good primer does not need to be entirely antagonistic to water. In fact, one can well imagine one which has smaller polar properties to water and will be adsorbed with like energy by the mineral surface. Its molecular weight should be considerably higher than that of water, but its molecules should have sufficient electrical likeness to those of water to permit a certain miscibility, which in customary fashion should decrease with decreasing temperature. Such a prime would partly substitute and dissolve the adsorbed moisture film. Owing to its lower water solving power at low temperatures, there would be no increase of the amount of moisture around the mineral; because of its higher molecular weight and its similar electric properties it would slowly substitute all the water molecules adsorbed on the mineral surface."

The answer to the above requirements seems to be the synthesizing of very thin films of artificial resins on the surfaces of the minerals. (22) Chemicals tried were furfural, aniline, a 3:2 mixture of aniline-furfural, a 2:3 mixture of phenol-furfural. Especially successful was a furfural-phenol type of resinification product. The aggregate is wetted well by components of the artiticial resins, and this makes for a better adhering and more uniform hydrophobic film. For best results heating to 100°C. is desirable although not essential. A. S. Janssen studied the effectiveness of precoating hydrophilic aggregate with furfural in preventing stripping of the binder in bituminous surfacings. (11) The effectiveness is very marked when the aggregate is precoated with 0.28 per cent by weight of furfural. The application of furfural to the wet aggregate is less effective.

G. W. Eckert states that methods of improving adhesion include incorporation of aluminum-oleate, "red oil", and light lubricating oil with aggregates and binders of the usual type; precipitation of an insoluble soap on siliceous aggregate, by successive treatments with alkaline substances and saponifiable materials; and treatment of aggregates or binders with organic ammonia derivatives. (5)

R. J. Shaw also studied the adsorption of asphalt to minerals (21) and he gives a different explanation for the difference in behavior of hydrophilic and hydrophobic aggregates. He states that in hydrophobic aggregates the oxygen film is loosely adsorbed, while in hydrophilic aggregates it is tightly held. The adsorbed oxygen can be removed by coating the aggregate with a thin film of oil and allowing it to burn off in the drying process. The layer of carbon left forms a surface giving good adhesion with the bituminous binder. This is obviously less applicable to the case of soil stabilization where the soil aggregates are wet. N. Ewers states that the use of resin or varnish is good but expensive, and that even complete drying of the aggregate was ineffective but partial combustion of oil used in the dryer was good. (7)

The effect of emulsifiers on the adhesivity of bitumen is discussed by H. Kleinert. (12) A very definite effect was noted. Of the emulsifiers tested resin, pine tar, and two products (unnamed) prepared in their laboratory appeared to give better results than tall oil (by-product from chemical wood-pulp) and fatty acids. In some emulsions, the adhesivity is impaired by excess emulsifier while in others it is improved. To obtain good adhesivity, the emulsion water must evaporate completely, it is stated.

The latest development in the use of bitumens for soil stabilization appears to be the addition of small percentages of paraffin wax. The Road Research Laboratory, Harmondsworth, England, has indicated* that the use of waxed bitumen for soil stabilization shows great promise. J. S. Jackson initiated the idea: "Briefly, the main object of the process is to establish the optimum conditions as regards water content and clay content (functioning as cohesive binder), and maintain these conditions more or less indefinitely by waterproofing the system by the addition of a small percentage of a suitable oil containing a minimum percentage of paraffin wax. Four per cent of paraffin wax is normally used with straight petroleum oils, while as little as two per cent will suffice with certain cracked products. (10) Jackson demonstrated the rigidity, both in compression and in two-demensional shear, imparted by the addition of paraffin wax to bitumen, when the latter is spread as a film on water. The Road Research Laboratory in a recent study (29) concluded that the difference in the waterproofing behaviour exhibited by waxed and unwaxed bitumens is thus probably attributable to the rigidity of the film due to the presence of the wax. (29) It is noted further that whereas in the case of unwaxed bitumen the amount of water absorbed by the treated soil increases as a linear function of the air-voids content of the soil, in the case of waxed bitumen the percentage of air-voids has little influence on the water absorption. (29, p. 1)

George W. Eckert made some very comprehensive surveys of developments in bituminous road materials which were published in the Proceedings of the Association of Asphalt Paving Technologists. (4) The scattered references that have been covered in our report will merely serve to indicate the nature of the results that have been achieved by research efforts directed at the improvement of various properties of bitumens. Mr. Eckert's reviews cover both the patent literature and the periodical literature, and are believed to be

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* By personal communication.

essentially complete reviews of all the literature appearing in the years that are covered by the reviews. Those interested in getting a really complete survey of all literature on bitumens in their relation to soil stabilization and road construction should use these reviews for the years for which they are available, and should scour patent and periodical literature of other years in a similar manner. The field is indeed too vast for comprehensive coverage in a summary report.

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Reference is made with the permission of the Director of Road Research.

RESINS

The use of resins, both natural and synthetic, in soil stabilization or soil solidification is relatively new. Theoretical concepts involved are as yet presented merely in the form of conjectures and hypotheses. As a result, no simple theory of the action of resins in soil solidification can be presented as was done in the case of the simple salts, calcium chloride, etc. The complexity of the resin--especially the natural resins--combines with the complexity of soils to render a theoretical study difficult at present. The field seems to offer such promise, however, that detailed mention of the work done to date must be made.

Natural Resins, Stabilizing Agents

Investigation of Soil Stabilization with Vinsol Resin: Vinsol resin is a powdered, brown, resinous substance obtained from an extraction process of pine stumps with benzol. A detailed description of it is given in Appendix I of an unpublished report from the Road Research Laboratory, Great Britain. (11c) It is virtually insoluble in water. Its pH value is 4.4. (15,p. 3)

The use of Vinsol resin as a soil stabilizer rests in its ability to act as a water repellent. A slurry of the proper amounts of Vinsol and water is prepared, using a small amount of caustic soda (20% of the weight of Vinsol used) as a dispersing agent and is distributed evenly over the area to be treated. The soil is then mixed and compacted by conventional methods. Vinsol has also been used as a waterproofing agent in combination with solidifying treatments of low water stability, as for example with aniline-furfural resin. (See page 57)

The action of Vinsol as a water-repellent has been the subject of much study. It was early conjectured that the action of the Vinsol slurry appears to be one in which the substance acts as a seal, thus causing the rise of capillary water to be retarded somewhat, rather than as an agent reducing capillary rise by increasing the angle of contact of the meniscus between it and the grains of the soil, although some reduction of capillary rise by actual increase of the angle of contact is possible. (14, pp. 2, 15, 16, 26) "As visualized, the Vinsol combines mechanically with water to form a Vinsol-water film around each soil grain. The characteristics of this film are such as to prevent additional water from entering the voids." (14, pp. 4, 5) Subsequently, on the basis of carful study, the Road Research Laboratory, Great Britain, stated: "Evidence has been obtained that materials of the rosin type (including Vinsol resin) probably form a monomolecular layer over the water film surrounding the soil particles, the hydrophobic parts of the molecules being orientated outwards so tending to reduce the capillary forces causing absorption of further water very considerably." (11b, p. 1) This is further discussed on page 42, No. 11.

The investigations made on the use of Vinsol as a stabilizing agent have brought out the following major points. It must be noted that although some of the points may seem contradictory, closer study of particularities of the actual soils used by the different investigators is necessary before any such assertion can be made.

(1) "The unconfined compression strengths of the raw and Vinsol-treated soils are for all practical purposes the same for the same condition of test water content." Vinsol is evidently not a solidifying agent. (14, pp. 2, 25, 29) It is reported that "the mechanical strength in shear of untreated brickearth soil has been compared with that of the same soil treated with Vinsol resin; it is shown that the angle of internal friction and the cohesion are both unaffected by the addition of small amounts of resin up to one per cent." (11f, p. 1)

(2) The range of soils effectively treated is limited. "It was found that a sandy silt, silty sand, clay silt, silty clay, and clay sand were improved considerably by treatment with Vinsol in the proper amounts, but that a silt and a clay could not be stabilized for the range of treatments studied." (14, pp. 1, 27, 28) "Vinsol resin was effective in waterproofing all the types of soil tested including the crushed chalk but was not effective with the cohesionless sand." (11b, p. 11)

In general, this indicates that Vinsol resin does not add cohesion to the soil; hence the bonding clay component and well-graded soil seems to be necessary. As stated above, the water repellent action of Vinsol seems to be based on the formation of a thin adsorbed film around the soil particles. This is further borne out by the fact that by allowing the compacted treated soil to "dry back" before exposure to free water, a higher-strength base results. (14, pp. 1, 29)

Note that the small quantities of the dispersing agent, caustic soda, commonly employed with Vinsol, did not affect the compaction characteristics of the molded soil. (14, p. 8)

(3) Beyond a certain amount of Vinsol treatment, no material change in water absorption is effected. (14, p. 10) A research project carried out by the Road Research Laboratory,

Great Britian, reports the following results using a clay loam soil. "The tests showed that small quantities (1%) of Vinsol resin are effective in reducing water absorption and that the use of greater amounts up to 12 per cent gave very little improvement." (11a, p. 1)

It was feared that in the case of Vinsol resin, the decrease in dry soil density with an increase of resin treatment might result in poorer water resistance due to the increased percentage of air-voids. Consequently, the water absorption of soil treated with surface-active stabilizing chemicals was investigated. (11f, p. 1) "These waterproofing agents were found to be of two types. In the first type (Oleine Oil, unwaxed bitumen), the amount of water absorbed by the treated soil increases as a linear function of the air-voids content of the soil. In the second type (Vinsol resin, gum rosin, waxed bitumen), the percentage of air-voids has little influence on the water absorption under the conditions of the test."

This strengthens the belief that the water-repellency is achieved through the formation of a thin resinous film surrounding the particles, and the explanation of the waterproofing properties of the materials is believed to involve questions of film structure. In the case of Vinsol, the molecules are rather large (molecular weight approximately 450) and the film may be solid. (11f, p. 4) A discussion is presented which indicates that the resistance to water absorption imparted by a material to soil is a function of the rigidity, or more exactly the compressive strength of the film it produces when spread on water. (11f, p. 5) "It would seem reasonable to assume that films of large molecules, like those of Vinsol, would be able to withstand larger compressions than films of fatty acid molecules with molecular weights of up to 200, although much will depend on the geometrical configuration of the molecules themselves." (11f, p. 5)

(4) The Vinsol treatment does not change the compaction characteristics of the soil at all appreciably. When soil, stabilized with Vinsol resin (and also gum rosin, waxed bitumen, cut-back bitumen, and oleine oil/methanol mixture) is compacted in the standard manner at optimum moisture content, "the stabilizer added merely takes the place of water and no additional air is trapped in the soil." (11f, p. 8) One investigation reported that treated soils in general had slightly higher optimum water contents (1-4%) than the raw soils. (14, pp. 19, 28) On the other hand, it is reported that "the addition of one per cent of Vinsol resin to brickearth reduces the maximum dry soil density obtainable under standard compaction by 2-3#/cu. ft. The optimum moisture content remains the same as for untreated soil. (11f, p. 8)

There is no strengthening action such as might be achieved by an increase in the maximum dry density through an increase in dispersion. In general, the compacted density of the test specimens decreases with increasing Vinsol resin content, and this is undesirable. "For any small percentages of Vinsol resin (0 to 0.5%) there was a tendency for a slight increase in density and this was marked in the case of the cohesionless sand." (11b, p. 11)

(5) "Of those soils that were benefited, the clay sand showed the greatest degree of stabilization and the silty clay the least." (14, p. 27).

This stands in line with the idea presented. The clay component acts as the binder; then in the case of sand, there is much smaller surface area for the Vinsol resin to coat than in the case of the silt. Note that the reason why an excessive treatment with Vinsol decreases the stability is probably connected with the fact that as the clay particles also become coated they lose their binding power.

(6) Alternate wetting and drying of samples increased the water repellency slightly, with little additional benefit noticeable after a second cycle. It appears as though the complete oriented adsorption of Vinsol on the surface of the soil particles takes place on first drying, and this is quite reasonable. (14, p. 29)

(7) It is apparent that the addition of a little alkali to the soil-resin system has a beneficial effect. Whether this influence is due to the formation of a complex salt of the alkali with the Vinsol, or only to a better dispersion of the resin, is not known. (10, p. 8)

(8) An investigation was made of the effect of the hydrogen ion concentration in soil water on the waterproofing action of resinous materials, since indications were that alkaline soils (with pH greater the 7.0) are unsuitable for resin stabilization. (11i) The investigation was mainly concerned with Vinsol and gum rosin.*

The pH value of an acid sandy loam was varied from 4.0 to 9.0 by addition of suitable amounts of calcium hydroxide powder and caustic soda solution. "The results show that the resistance of the specimens to water absorption was effective over the pH range 4.0 to 6.5, but that at pH values of about 7 absorption of water increased, presumably due to the breakdown of the resin film. With calcium-modified soil, some waterproofing occurs above pH 7, which may be due to the formation of a film of insoluble calcium resinate on the soil-water/air interface. From pH 7.2 to pH 9.2, the waterproofing decreases linearly with increase in pH, the decrease being

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* See page 45 .

more marked with the rosin than with Vinsol resin treated specimens. In the case of sodium-modified soil, most of the specimens with pH greater than 7 collapsed after seven days although the numerical values of the water absorption were not unduly high. It is considered that in these circumstances the free sodium hydroxide present in the soil water would attack the stable resin films and form freely soluble sodium resinates."

(Note. "In passing from an acid to an alkaline reaction, the flocculation or state of aggregation of the clay particles might possibly change, and with it the water absorption characteristics of the untreated soil." Determination of liquid limits on untreated samples and samples with one per cent calcium hydroxide, and one per cent sodium hydroxide indicated that such effects were negligible.) (11i, p. 4)

Resinous materials of the type considered in these experiments (i.e. those in which the polar orientation at the soil-water/interface is due to the carboxylic (-COOH) grouping in the molecule) are fully effective only when applied to acid soils, since it appears probable that the breakdown of the resin film at pH values above 7 is due to the formation of alkali resinates. This view of the mechanism may hold only for the sodium-modified soil since sodium salts of Vinsol and gum rosin are known to be water-soluble. Calcium salts, on the other hand, might be expected to be insoluble "and it is further known that the presence of calcium or barium ions in the substrata has a 'solidifying' effect on long-chain fatty acid films." (11g, Table I, p. 4)

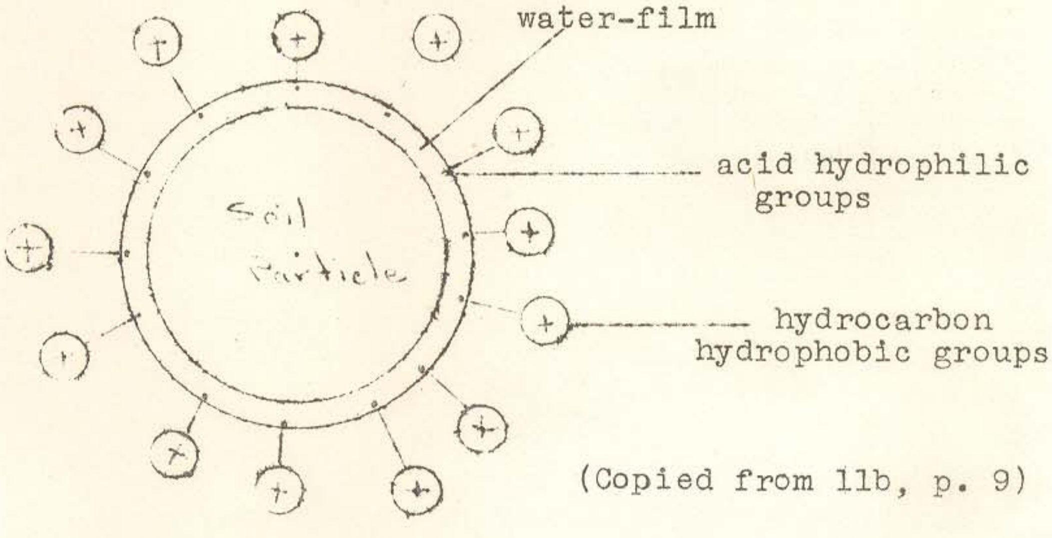
It is suggested that the substitution of aldehydic (-CHO) or primary alcoholic ($-CH_2OH$) groupings for the polar carboxylic (-COOH) groupings in the resin molecules might overcome the deleterious effects of alkaline reaction in the soil water. (11i, p. 1)

(9) Insoluble Vinsol resinates prepared by the flocculation of an alkali resinate with iron and aluminum salts are considerably more effective stabilizing agents than untreated Vinsol. (10, p. 8; 15, p. 16)

(10) "For practical purposed the waterproofing properties of Vinsol resin were unaffected by the method (powder or slurry) by which it is applied to the soil or by the moisture content of the soil at the time of mixing. The water absorption was found to depend upon the compacted density with both Vinsol and bituminous stabilizers. (11a)

(11) Four points emerge from consideration of the results of an investigation on the water absorption of soils treated with resinous materials. (11b) a) "Vinsol resin does not act merely by virtue of dispersed particles of water repellent material." b) "Vinsol resin is much more effective than would be expected from simple contact angle measurements." (Author's note: these contact angle measurements were made on Vinsol in the bulk state) c) "The effectiveness of Vinsol (or rosin) was not found to decrease with time over the period covered, even though the contact angle of water against Vinsol decreases with time." d) "The presence of some water is necessary before the Vinsol becomes effective in reducing the rate of absorption of further water by the soil."

"All these points support the view that Vinsol resin in some way spreads as a film over the surface of the water that coats the soil particles and this film has considerable water-repellent properties towards the incoming water;" the mechanism is probably as shown in the sketch below.



(Copied from 11b, p. 9)

Note that this being the case, about 0.1 per cent Vinsol of the weight of soil should be effective enough since that is about all that would be required to form a mono-molecular layer over the water coating of the soil particles. This hypothesis was confirmed. (11b, p. 9) It is, therefore, indicated that the use of appropriate admixing methods for treating soils with Vinsol is important, if for no other reason, at least to reduce, by achieving good dispersion, the amount of resin necessary for optimum water repellency.

The investigation of contact angles was subsequently furthered (11e). "The contact angles exhibited by water against Vinsol and rosin were considerably higher when the materials were deposited electrolytically on aluminum than when the materials were tested in the bulk state by spreading the molten materials in their films or glass slides." (11e, p. 1) It may be noted that testing in the bulk state cannot be considered a fair test if the mechanism of waterproofing is that of oriented adsorption of the molecules on water films: electrolytic deposition on the other hand, may achieve the necessary oriented adsorption of the resin molecules. Accordingly, it was found that "the order of magnitude of the contact angles exhibited by water against Vinsol resin and rosin deposited on an aluminum surface is that which would be required if mono-layers of these materials are to produce waterproofing in soil by a contact angle mechanism. Also, these contact angles are numerically in the order of the known relative waterproofing efficiency of the two materials." (11e, p. 1) Caution is necessary in using results of contact angles of material deposited on an aluminum slide for anything but general indications, since with the electrolytic deposition "the forces binding the molecule in the soil system and consequently a tighter packing would be expected in the case of the deposited films." (11e,p.5)

(12) "The waterproofing action of Vinsol is not seriously affected by drying out of the soil mass." (11b, p.2)

(13) The effects of curing on the water absorption characteristics of treated soils has been studied. (11c, p.1)

"Specimens made with one per cent Vinsol resin and brickearth compacted at optimum moisture content to a density of 112#/cu. ft. of dry soil, show no reduction in water absorption after curing periods up to seven days. If, however, the soil density is reduced to 98#/cu. ft. of dry soil, corresponding to an increase in air voids from 9 per cent to 23 per cent, the period of curing has a noticeable effect on the water-absorption." (11c, p. 3)

Work carried out at the Department of Colloid Science at Cambridge showed that Vinsol resin gives off a "condensed" film on the surface of water very slowly.* (11c, p. 4) The maximum surface pressure as measured on the Langmuir trough

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* "A condensed film is one in which the film molecules have sufficient mutual attraction to lie on the water surface in 'islands' if the area of water surface is too large for the available molecules to cover. Condensed films are characterized by a sharp rise in the force/area relationships as measured by a Langmuir trough, corresponding to a point at which all the available surface has been covered by a monomolecular layer. (11c, p. 4)

was found to be 10 dynes/cm. for Vinsol. "Surface tension measurements showed that Vinsol resin reduces the surface tension by only 0.25 dynes/cm. when spread at a rate of two mgs. per 100 sq. cm. of surface." These factors are related to the water-repelling action of Vinsol, as will be discussed under "321". (see page 51 of this report.)

(14) Winn and Rutledge found that the addition of small quantities of Vinsol resin (1 to 5%) considerably reduces damage caused to soil specimens by freezing. The resin was generally found to increase in effectiveness after a period of curing. (8) This is confirmed for a crushed run chalk. (11c, p. 5)

The fact that the resistance to frost action increases with curing time suggests that this resistance may arise from the same cause as the resistance to water absorption, i.e., to the resistance of movement of water in the pores of the soil that is imparted by the stabilizer. (11c)

(15) An investigation comparing the waterproofing effectiveness of two resinous materials (Vinsol and gum rosin) and two water-soluble industrial detergents (cetyl pyridinium bromide and sodium alkyl sulphate) brought out the following points. (11g, p. 1)

a) The surface tension as measured by a film-tension method (and hence the spreading pressure) of the material "had no relation to the final waterproofing properties of the material, although in the case of the two resins, the reduction of the surface tension by about 10 dynes/cm. brought about by gum rosin may influence the initial amount of water absorbed." (Vinsol showed no reduction of surface tension, within the limits of accuracy of the experiment.) This is discussed at length. (11g, p. 6)

b) The resinous materials caused no appreciable reduction in the heat of wetting which further supports the theory that there is no adsorption of the resins on to the surfaces of the soil particles. Further evidence for this point of view is found in the shapes of the stabilizer-content water-absorption curves; the smooth curves are consistent with the mechanism of waterproofing achieved by means of a surface film spread out over the surface of the incoming water. "Such a film would be spread over the entire cross-sectional area of the soil cylinder and would not be dependent on local variability of dispersion of the resin." (11g, p. 6)

(16) Another investigation on the mechanism of water repelling of resinous materials reports differences in behaviour between Vinsol resin and rosin on the one hand and a

mixture of fatty acids, and a mixture of 70's Oleine oil and methanol on the other hand. (11c, p. 1)

Reference to the results reported on Vinsol resin and Rosin has been made on page 42, No. 11. "The contact angles exhibited by water against unsaturated and saturated fatty acids deposited on aluminum surfaces are higher than those exhibited by the resinous materials considered, although their behaviour as soil waterproofing agents is known to be inferior to that of the latter. This supports other evidence that the waterproofing of soil achieved by these two groups of materials is brought about by different mechanisms to that obtaining with the rosin group of materials." (11e, p1).

(17) Preliminary investigations on bacterial attack of resin stabilized soils report the following results. (11h, p. 1)

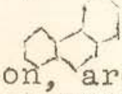
a) "Some soil bacteria and fungi are capable of attacking the two resins used (Vinsol and gum rosin)."

b) "The presence of these resins in the soil produces an increase in the number of micro-organisms present; in particular, those that attack resins and which may contribute to road breakdown."

c) "For the purpose of the selective counting of organisms that attack resins, selective counting media have been developed."

(18) Results are reported of the stabilization of Norfolk sand with Vinsol dissolved in acetone and in approximately normal solution of sodium hydroxide. The use of 4.0 per cent Vinsol in acetone gave very good results which indicate that Vinsol dissolved in acetone is a solidfying agent comparable to the other resins. The Vinsol in sodium hydroxide behaved poorly. (1, p. 34)

Soil Stabilization By the Use of Rosin: The earliest mention of the use of wood rosin in road construction seems to be the article "Rosin in Road Construction (Russia)". (13) Satisfactory results were obtained when sandy soil was treated with wood rosin, a 70:30 mixture of hard rosin and crude rosin, and peat rosin: the mixed rosins proved best. Much more recently Mr. A. B. Miller (Hercules Powder Company) patented the invention in this country claiming the possibility of stabilizing soil by mixing therewith a saponified, substantially petroleum-hydrocarbon insoluble pine wood rosin. (6)

Rosin is obtained from pine stumps and top wood. The chemical composition is given as mostly abietic acid, $C_{20}H_{30}O_2$, (about 90%) and a small amount of non-acid materials called resenes. (10) Abietic acid has a partially hydrogenated phenanthrene nucleus of the form  . (11d) It "forms salts with sodium hydroxide and potassium hydroxide which, upon complete neutralization, are soluble in water in low concentration, but form gels at higher concentration. Ammonium rosinates in aqueous solution have a greater tendency to gel formation than the sodium or potassium rosinates. It is claimed that oxidation of the rosin favors the formation of ammonium rosinates. Rosins form insoluble salts with bi- and tri-valent metal ions." The acid number, which represents the milligrams of potassium hydroxide needed for rapid neutralization of the rosin acids contained in one gram of rosin, for the rosins (Grade B and Belro) used in the investigation was about 158. (10, p. 2,3)

The most noteworthy results of investigations on the soil stabilizing effectiveness of wood rosin are the following:

1) The soil stabilizing power of rosin increases with decreasing particle size of the rosin. (10, p. 1)

2) Soils in the intermediate range, i.e., those not containing an excess of sand or an excess of clay, were most benefited. It is not clearly determined whether this is merely an effect of better gradation or whether this is in line with results that would be expected in view of film formation, as in the case of Vinsol. (10)

3) "The stabilizing efficiency of rosinous materials had been found to depend on the degree of dispersion in the soil system and on the water affinity of the deposited material. Tests were, therefore, made in which the rosin was first dispersed in the soil as a more or less water soluble compound and then rendered insoluble by exchange reaction with salts of bi- and tri-valent metals." As would be expected, the rosinates formed by the use of iron and aluminum salts were the best stabilizing agents. (10, p. 6)

4) "There exists an optimum ratio of alkali to rosin with respect to stabilizing power. For the sodium and potassium rosin compounds this ratio appears to correspond to the complex salt: one rosinate--three rosin acids." (10, p. 1) For the ammonium rosin compounds good results are obtainable over a wider range of composition, probably because of the volatility of ammonia. "The volatility of the ammonia affords a distinct advantage over the other alkalis, in that it acts as a good dispersing agent which after drying does not leave a soluble and water-attractive residue behind." (10, p. 6) The experiments conducted with $(NH_4)_2CO_3$ did not give as good results as those conducted with the hydroxide: this is not fully understood.

5) Best resistance to wetting-and-drying was obtained when the alkali-acid number ratio was about 1:4. However, best resistance to freezing-and-thawing was obtained when the alkali-acid number ratio was about 1:1. "These results may be explained by the fact that the reaction between alkali rosinates and metal salts results in the formation of soluble salts that possess a great affinity for water. The quantity of these salts present is proportional to the amount of alkali and salt used. While this property of the salt lowers the resistance of the soil to wetting and drying, in the case of freezing and thawing tests it tends to bind the water so strongly that it does not freeze and, therefore, the system is less affected by low temperatures." (10, p. 7)

6) See No. 14 on Vinsol.

7) See No. 15 on Vinsol.

8) See No. 8 on Vinsol.

9) In general, statements made under Resin 321 are applicable. (Pages 49-52)

Winterkorn offered the following thoughts as hypotheses of the stabilizing action of this treatment.

Firstly, the dispersing action of the alkalinity aids in compaction to greater densities. (The Road Research Laboratory, however, notes that "all the stabilizing agents containing rosin or rosin derivatives reduced the density of soil obtained for a given amount of compaction." (11d) These tests used a brickearth.) A possible transfer of sodium ions from the resin to the clay particles may further act to reduce permeability.

Secondly, "if the rosin substance enters into any direct reaction with the soil constituents at all, the most probable reaction is with the exchangeable ions. This reaction would result in a decrease of the accessibility of these ions and, therefore, in a decrease of the attraction forces for water. It is not suggested that all the water attraction centers on the soil constituents are shielded by the stabilizer; rather, a certain number of these must be considered unshielded or only partially shielded in order to account for the cohesion and the consistency properties of the treated soils." (10, p. 7)

In a comparison of the action of various resinous materials, the Road Research Laboratory, Great Britain, reports that resinous materials, including rosin and rosin derivatives, powdered crystal rosin, and a stabilizing agent C 40244, containing chemically combined rosin (submitted by Messrs. Imperial Chemical Industries, Dyestuffs, Ltd.) behaved in a similar way. Powdered rosin is more effective than Vinsol; C 40244, about equivalent to Vinsol. (11b)

This study of the comparative effectiveness of various soil waterproofing agents was continued. (11d) The waterproofing agents investigated fall into three general classes, as listed below.

(a) Stabilizers containing rosin or rosin derivatives, and therefore presumably containing a phenanthrene nucleus.

C.46707	A mixture of sodium rosinate and aluminum sulphate. (powder)
XP.64	A 25% aqueous solution of sodium rosinate. (Equal volumes of a 20% aqueous solution of aluminum sulphate were subsequently added in all cases.)
C46708	A mixture of sodium rosinate and aluminum rosinate. (powder)
C.46709	A mixture of gound rosin and sodium aluminate. (powder)
C.46710	A mixture of sodium rosinate and sodium aluminate. (powder)

(b) Stabilizers containing saturated aliphatic compounds.

C.46711	A mixture of fatty acids and mineral oil. (liquid)
XP.60	An aqueous solution of the sodium salts of mixed fatty acids. (Equal volumes of a 20% aqueous solution of aluminum sulphate were subsequently added in all cases.)

(c) A stabilizer containing unsaturated aliphatic compounds.

XP.63	A mixture of 70's oleine oil and methanol (liquid). (Oleine oil is largely composed of oleic acid.)

These soil stabilizing agents were compared with Vinsol and Resin 321.

"It was found that the stabilizers containing rosin or rosin derivatives gave the most satisfactory results, being in general equal in efficiency to Vinsol and Resin 321." The XP.64 was the best and "the amounts of sodium rosinate and aluminum sulphate required to produce a given degree of waterproofing, when applied as aqueous solutions, were found to be only a quarter of the amounts required when the powdered materials were used." Aliphatic compounds were definitely inferior.

Use of Resin Stabilizer 321*: Resin Stabilizer 321 is a complex salt corresponding to one molecule of sodium abietate and three molecules of abietic acid. Use of this resin in stabilization is patented. (4) "By removing abietic acid from rosin by dissolving rosin in alcohol, and then adding an alkali in amount sufficient to form sodium tetra-abietate or sodium acid abietate, a substance is obtained which is insoluble (relatively) in most pure solvents. The invention contemplates rendering soils water-resistant." Resin 321 is a finely powdered white resinous substance, exceptionally light, not hygroscopic, possessing a low water affinity. The acid number is about 130. Its pH is 6.3. (15, p. 3) "It should be kept in mind that R-321 is not an unique material but only one member of a large family of actual or possible resinous stabilizing agents." (2, p. 14)

"Treatment with Resin 321 reduces the moisture absorption of soils. This reduction pertains not only to the total amount of water absorbed but also to the rate at which this absorption occurs." The latter effect is the more important. (2, p. 9)

The following theoretical concept of the stabilizing action of Resin 321 has been presented by Hans F. Winterkorn. (2, p. 13) "Because of its alkalinity and spontaneous dispersion into ultramicrons in contact with water, the stabilizer may exert a dispersing effect on the treated soil," thus aiding compaction. "Further, a decrease of the permeability of the soil can be expected by transfer of sodium ions from the stabilizer to the soil."

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* Although Resin 321 and Stabinol (p. 52) are rosin derivatives, they are being given separate mention here because somewhat more detailed work has been done on them. It should be borne in mind that statements made about the action of rosin derivatives apply to Resin 321 and Stabinol too.

"After or while fulfilling the function of making a soil less pervious, the stabilizer becomes irreversibly changed in such a way that it loses its dispersing power." "A great number of reactions may and probably do occur either singly or in unison. The irreversibility may be caused by exchange reaction between the sodium and the hydrogen ions on the stabilizer and the hydrogen and other adsorbed ions on the soil particles. The type and amount of humus in the soil undoubtedly play a role in this connection. The irreversibility may also be caused by purely physical adsorption phenomena, or by any and all physical or chemical surface phenomena which are known to play a role in soils. In this connection, the importance of microbiological phenomena must not be overlooked." (Cf. Vinsol No. 8) (2, p. 13)

"This fixing of the stabilizer by the soil occurs already in the moist medium; however, drying accentuates this fixing by inducing the complex molecules of the stabilizer to orient their inorganic hydrophilic faces towards the inorganic soil particles and their hydrophobic resinous ends toward the atmosphere. Becoming fixed in this position, the stabilizer shields the water attraction centers on the soil particles and does not permit easy wetting of the system." (2, p. 14) The reader is here referred to the discussion of the waterproofing action of Vinsol resin and gum rosin and rosin derivatives, pages 37, 41, etc.

Some of the observations made in investigations of the stabilizing action of Resin 321 are presented herewith.

a) The increase in effectiveness of 0.5 per cent of Resin 321 over 0.2 per cent, as measured by their "bearing ratios" and by water absorption tests was not proportional to the amount of admixture used, except with a soil which had a high percentage of clay. With one exception, (reason for erratic behaviour unknown) it seems to be true that the soils with relatively high percentage of sand (and corresponding low base-exchange capacity) reached their optimum of amount of treatment at about 0.2 per cent. The more plastic soils, with higher per cent of clay and corresponding high base-exchange capacity, required more resin treatment to achieve optimum stabilization. (2, p. 7)
(Note. The experimental results presented are unsuited to the determination of the separate effects of different variables.) The decrease in the per cent of absorption was most pronounced in the less plastic soils. (2, p. 7)

b) In all cases of treated soils, drying of the specimens previous to soaking decreased their final water content in water adsorption tests. (2, p. 7)

c) In unconfined compression tests after seven days of soaking in water, it was found that the more sandy soils, none of which lacked the necessary binding clay fraction, showed the highest strengths. (2, p. 8)

d) In the unsoaked condition both the treated and untreated specimens of more plastic soils showed considerably greater strengths at the lower moisture contents than did the more sandy soils, and the moisture content-compressive strength relationship is practically independent of the percentage of treatment. (2, pp. 8,9) This is as would be expected if the clay's action as a binding agent were not impaired. The stabilizer does not add to the cohesive properties of the soil. (2, pp. 1, 14) It must be noted also that for equal water contents, a specimen which had been dried back from a higher to a lower value showed greater compressive strength than one which had reached the same water content from the dry side by absorption; this phenomenon occurs in most types of stabilized soil, and is probably due to the predominating effect of rates of absorption in damage by wetting. (2)

e) A slightly acid reaction in soil is favorable to the action of Resin 321. (Cf. Vinsol, No. 8) (2, p. 12)

f) Dry-land organic matter may be very helpful in the stabilization of soil in contrast with wet-land organic matter which is usually detrimental. (2, p. 12)

g) Resin 321 gives off a condensed film on the surface of water very slowly. "The surface activity of 321 was found to be much greater than that of Vinsol, and the maximum surface pressure as measured on the Langmuir trough was found to be higher," i.e., 16 dynes/cm. (11c, p. 4)

As in the case of Vinsol, in specimens of relatively low density, curing decreased the water-absorption, although the curing time is shorter and the reduction in water absorption is not so marked. "The final water absorption reached by specimens treated with 321 is much lower than that attained by Vinsol treated specimens containing approximately the same amount of air-voids." (11c, p. 4)

"It is possible that the higher surface pressure of 321 resin may account for the shorter time required to attain maximum resistance to water absorption, but the resin 321 is more effective than would be expected if this were the sole reason, and no conclusions can yet be drawn." (11c, p. 4)

h) Finally, tests were also made using admixtures of aluminum or ferrous sulphate with the resin 321. Tests were performed using 0.25, 0.50, and 1.0 per cent of 321, with each per cent of 321 mixed with 10, 20, and 40 per cent aluminum or ferrous sulphate (by weight of 321). The results showed that such admixture was very advantageous, the effectiveness of each sulphate chemical being the same. (15, p. 16) This effectiveness is in no way based on advantageous changes of the pH of the soil. (15, p. 17)

i) "The optimum amount of stabilizer probably lies between 0.2 and 1.0 per cent, the optimum increasing with the amount and activity of the clay contained in the soil system. Experiments made with Resin 321 and similar resin complexes of higher alkali content indicate a shifting of the optimum amount required toward smaller values with an increasing alkali content of the stabilizer." (2, p. 10)

Stabinol: This material consists of three parts of Portland cement and one part of either unrefined complex salt 321 or a complex salt consisting of unneutralized abietic acid, sodium resinate and calcium resinate. It is grey powdered material, which can be handled like Portland cement. It has a pH value of 11.1. (15, p. 3)

"In contrast to the apparent ineffectiveness of 321, it was found that Stabinol successfully waterproofed all soils tested." (15, p. 7) This apparently is not merely an effect of the Portland cement: the waterproofing given by the 321 is essential. Note, however, that in wet-dry cycling the Stabinol did not prove as effective as 321. (15, p. 15)

Probably because of its Portland cement content, Stabinol seemed to be most effective with sands, sandy silts, gravelly clay sands: It did not work at all well with clayey silts and silty clays. (15, p. 19)

NSP-121: An experimental powdered resinous material made by the National Southern Products Company. It is a mixture of complex organic acids partially neutralized with hydroxides of alkaline and alkaline earth metals, and has a pH value of 8.0. The company claimed that certain soils required only 0.25 to 0.50 per cent treatments for satisfactory water repellency. This was not confirmed, since even one per cent failed to give satisfactory results, although some improvement was noted. (15, p. 24)

NSP-25-2: This product is also made by the National Southern Products Company and is a mixture of a mineral carrier and of fatty and resinous acids partially neutralized with hydroxides of alkali and alkaline earth metals. It has a pH value of 11.8. A one per cent treatment of this proved effective on a sandy silt. Two clayey silts showed considerable improvement, but were not satisfactorily enough stabilized. (15, p. 24)

NVX: This product, made by the Hercules Powder Company, is understood to be neutralized Vinsol resin (probably neutralized with a mixture of sodium and calcium hydroxides). It has a pH value of 9.6. This also only proved satisfactory with a snady silt. Two clayey silts showed considerable improvement, but were not satisfactorily enough stabilized. No improvement was noted on a gravelly clay sand. (15, p. 24)

It must be noted that evaluation data on these stabilizers is scant. The conclusion reached from a field test was: "Stabinol appeared to be the best all-around water repellent. Next in order were 321 in combination with ferrous sulphate, 321 only, and Vinsol with caustic soda, all of which performed with about equal effectiveness. NVX and NSP-25-2 were satisfactory and were equal in performance, but were not as efficient as the other repellents." (15, p. 25)

Lignin Liquor; (Sulfite lye, sulfite waste liquor, lignin extract, etc.) Scattered mention has been made of the use of this material for soil stabilization. According to an anonymous article in Roads and Streets, lignin liquor is used as a binding material and may be sprayed. (12) Lignin liquor is also discussed by A. B. Miller of the Hercules Powder Company, who states that soil can be stabilized by the addition of lignin or ligneous materials. (5)

Lignin liquor is a resinous alkali waste liquor produced in the paper industry. Its waterproofing properties were studied in investigations on a group of materials of the resin type. (11b) It has a definite waterproofing action, although inferior to that of Vinsol. The superiority of the rosin-type materials arises from their characteristic surface properties when in contact with water. (See Vinsol)

It is claimed, by Guillaume Piette, (7) that there is a definite increase in strength with increase in quantity of lignin extract and that this increase is approximately proportional to quantity. Need to investigate waterproofing at higher lignin contents is indicated. The solubility of lignin is not an objection to its use as after drying the soil becomes practically waterproof to underground water.

Natural Resins from Tropical Areas: Six natural resinous materials from tropical areas have been investigated to determine their suitability as soil waterproofing agents (11). The resinous materials studied are: Wallaba resin, Manila Copal resin, Damar resin, Belgian Congo Copal resin, Hal resin, and Niger Paste. For a brief description of these resins, the reader is referred to the original report.

Only two of the materials showed any waterproofing characteristics: the sample of Manila Copal resin which was somewhat less effective than Vinsol resin, and the Wallaba resin which had some initial waterproofing effect, although this was neither comparable to that exerted by Vinsol resin nor operative for any length of time.

Investigation of the use of Wallaba resin was furthered with the anticipation that certain modifications of the molecular structure would improve the soil waterproofing characteristics by altering the surface active properties of the resin. Derivatives prepared with this in mind included the calcium salt and the acetyl and benzoyl derivatives. The acetyl derivative showed some improvement over the natural resin both in degree and permanency of the waterproofing effect.

C40242, C40243: C40242 and C40243 were stabilizing agents submitted by Messrs. Imperial Chemical Industries (Dyestuffs) Ltd. for investigation by the Road Research Laboratory, Great Britain. Data on these is too scant to warrant any discussion. (11b, p. 2)

The following general comments apply to all natural resin-type repellents:

1) The use of the pH value of a soil as a guide to determine whether a soil can be satisfactorily waterproofed by a resin-type repellent is not conclusive and is not recommended.

2) The repellents are not recommended for clean cohesionless sands and gravels. Resin-type repellents have great possibilities in the stabilization of sand-clays, sand-clay gravels, and similar base course soils of relatively high plasticity indices.

3) H. F. Winterkorn pointed out that soils containing little or no soluble material could generally be waterproofed immediately, whereas soils containing large amounts of soluble materials would require generally longer periods of time to be effective. The factors affecting the role of development

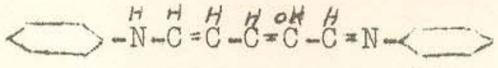
of the waterproofing action are: (a) base-exchange capacity (b) base saturation (c) type of exchangeable ions (d) total water solubles, which consist of salts, hydroxides, acids, and nonionic molecules (e) bacteria. Distinctly acid soils (pH 3-5) contain little or no soluble material as a rule, whereas distinctly alkaline soils (pH 9-11) contain large quantities of water-soluble materials. (16)

4) "In general, stabilizing admixtures that owe their effectiveness to a binding or cementing property are more affected by the freeze-thaw test than by the wet-dry test; for waterproofing admixtures, the reverse is true. This, of course, is a consequence of the use of cementing agents for noncohesive and of waterproofing agents for cohesive soils." (9, p. 11)

Synthetic Resins, Solidifying Agents

Aniline-Furfural Resins: Hans F. Winterkorn investigated the possibility of using certain synthetic resins for soil solidification (9). A review of the history and structure of aniline-furfural resins* is appended to the report on those investigations. (9, p. 15)

Of first concern was the determination of the best proportions of aniline and furfural for resin formation. The results of a series of tests established the existence of two desirable ratios of the components. The product obtained by using a ratio of one mole of furfural to two moles of aniline was the best resin obtained; its probable molecular structure is given as:



which structure "well indicates the polar nature of this substance which makes it easily adsorbed by the soil particles." (9, p. 2) The second optimum proportion coincided with a ratio of two moles of furfural to one mole of aniline; the probable structure of this substance is also briefly discussed. (9, p. 15) Finally, in certain tests the possible existence of yet another resin compound was indicated, corresponding to a composition of aniline and furfural in the ratio of 1:1.

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* Furfural and its resinous derivatives had been used for improving the affinity of hydrophilic aggregate for asphaltic bitumen. H. F. Winterkorn, Ind. and Eng'g. Chem., Vol. 30, p. 1362, 1938.

The possible effect of acid, alkaline and neutral media on the resinous cements was investigated. Neutral specimens showed a distinct maximum compressive strength at ratios of aniline-furfural of about 70:30 (corresponding to the first resin product mentioned above). Acid catalysed the reaction but decreased the maximum compressive strength, shifting the peak of the curve to a point corresponding to ratios of aniline-furfural of about 50:50. In alkaline specimens, the optimum point corresponded to the 70:30 aniline-furfural resin, but this optimum was very poor. The resin product of 35:65 aniline-furfural showed good dry strengths, but did not withstand attack by water. (9, p. 5)

The effect of different anions and cations on the quality of the 70:30 and 35:65 aniline-furfural resins was investigated, but no very conclusive or outstanding results were obtained. Cation treatments seemed to be detrimental, possibly because of alkalinity, since the cationic compounds were added in the form of hydroxides. None of the acid admixtures resulted in great improvement. Sodium silicate, investigated because of its possible cementing action and its possible catalyzing effect on the resin, was detrimental rather than beneficial. (9, p. 7)

In view of the fact that the 70:30 aniline-furfural resin offered the best promise, it was used for further investigations with various soils. The resin has considerable binding power; but no appreciable weathering resistance was obtained unless two per cent treatment (or greater) was used. In the amounts employed in the investigation, however, the effectiveness of aniline-furfural was mainly due to its waterproofing properties, although its effect on the sandy soil was obviously that of binding the particles. (9, p. 11) "The aniline-furfural resin compares favorably with cement in binding properties and, at the same time, performs as well as liquid asphalt in waterproofing the soils." (9, p. 12)

Suitable catalyzation for the reaction implied an increase of the induction period to prevent the spontaneous starting of the condensation reaction which tends to complicate admixing procedures. The search for an effective and adjustable catalyst for the aniline-furfural reaction was given due importance in the investigations. (9, p. 17) The major conclusions may be listed here:

1) The best catalyst found for the aniline-furfural reaction was aluminum chloride. $FeCl_3$ was a little less effective.

2) "The greater the amount of either of these catalysts used, the greater was the acceleration of the reaction."

3) "$BaCl_2$, $FeSO_4$, NaCl, PbO, and H_3PO_4 were tried as catalytic agents, but did not produce good results."

4) "The presence of large quantities of water was found to decrease the effectiveness of the catalysts. A soft, gummy resin was formed which tended to settle out at the bottom in tests in which the water was just stirred into the aniline-furfural mixture. However, if the water was emulsified with the aniline-furfural mixture, the resin formed as a flocculent precipitate."

5) "In cases where the samples were emulsified, it was found to be more practical to add the catalyst after the material had been emulsified."

6) "The addition of a small amount of soap was effective in keeping the reaction from taking place in the aluminum emulsifier." (9, p. 19)

Finally, the effectiveness of aniline-furfural resins in conjunction with Vinsol, Congo resins, and semi-solid amines, was investigated. The resin mixture was prepared by dissolving the Congo resin or Vinsol in furfural, then adding it to the soil. None of the mixtures gave as good results as the aniline-furfural resin alone. (9, p. 13) Specimens were made using a two per cent of aniline-furfural resin (25:75) in conjunction with two semi-solid amines (45% on the basis of resin added). The results showed no improvement over the control of two per cent aniline-furfural resin. (9, p. 13)

Other Synthetic Resins

Urea-furfural and phenol-furfural resins: These were tried alone, and in mixtures with aniline-furfural, or Belro Rosin. The results were poor. (9, p. 12)

Phenol-formaldehyde Combinations: Combinations of phenol and formaldehyde were tried, but specimens failed in water showing that the material did not set at the low temperature employed. The use of catalysts might be investigated. (9)

Urea-formaldehyde resins, including "Weldwood Glue": Several salt catalysts were tried. Direct acid-base catalysis was not attempted, but offers possibilities. (9) Another investigation of the use of urea formaldehyde resins included the study of Urac 103 and Urac 180 supplied by the American Cyanamid Corporation, and Weldwood supplied by U.S. Plywood Corporation. (1, p. 30) These are sold for use as waterproof glues. Urac 180 is in liquid form, and ordinarily requires the addition of an acid salt or other catalyst to induce setting. Urac 103 and Weldwood are dry powders in which buffers and catalysts are incorporated.

The test values of Urac 103 were rather low but probably adequate. The Urac 180 and Weldwood gave excellent dry strength and good wet strength when used in quantities of four per cent resin mixed with five per cent water, both based on dry weight of sand. Higher moisture contents were detrimental.

Calcium Sulfamate-formaldehyde Resins: Results so far have not been very good but the field is still to be investigated. The fact that the water insoluble resin is easily formed by an exothermic reaction may be helpful. (9)

Synthetic Resin Formed by the Interaction of Furfuryl Alcohol and Sulfuric Acid: This material gave very promising results in a laboratory investigation. The rate of resin formation is proportional to the concentration of acid employed, and experiments on a sand and fine sandy loam indicated that both the strength and the water resistance are proportional to the amount of treatment. Oven-drying increased the strength greatly. (3, p. 8)

Polyvinyl Alcohol (PVA): "Vinyl alcohol, $H_2C = CHOH$, has never been isolated and is known only in polymer form. It is obtained by hydrolysis of polyvinyl acetate. (1, p. 3) A series of polyvinyl alcohols having a range of solubilities, viscosities, film strengths, and other properties, may be produced by varying the degree of saponification and polymerization." The material was supplied by E. I. du Pont de Nemours and Company as a fine, granular white powder.

PVA forms very tough, flexible films upon evaporation from aqueous solutions. One practical advantage in the use of PVA is that it requires no organic solvents in its application. The difficulty is that the dry films soften and redissolve slowly in water. "In order to prevent the softening of PVA films by moisture, insolubilizers and water repellents may be added to the PVA solutions or directly to the soil." Four grades of PVA were tried: a high viscosity grade 391-B, a moderate viscosity 349-B, a low viscosity 393-B, and a low viscosity 623-A. The grade A material slaked upon standing in water, and the low viscosity type B material had a low water resistance. Subsequent testing was done merely with the high viscosity 391-B material which should be the most slowly leached from a wet soil.

The dry strengths with sand were very good. "At the highest moistures the PVA was concentrated near the surface of the specimen forming a hard tough outer layer with the center soft and crumbly," but this did not affect strength results much. PVA appears to be about equally effective in acid or in alkaline soils. (1, p. 39)

An effect that is not understood yet is the fact that the results with a particular sand were much better than with others. It was ascertained that this is not caused by presence of clay or colloid in the sand. (1, p. 12)

Since PVA is soluble in water, it loses most of its power to stabilize sand when wet. It is necessary, therefore, to insolubilize the PVA or to prevent it from becoming wet. (1, p. 13) The following table summarizes the search for materials that would give water repellency. (1)

Repellent	Quantity of Repellent Per Cent of PVA	Capillary Rise
Vinsol*	250 to 1000	None
Sodium stearate	5 to 30	None
Sodium oleate	10 to 30	None
Tung oil	15 to 30	None
Mexican oiticica oil	15	None
Saponified soybean oil	10 to 30	None
Saponified tung oil	5 to 30	Smm/24 hrs.
Ammonium acid stearate	5 to 20	24 hrs.
Linseed oil	15 to 30	none/1 hr.
Vinyl chloride-acetate	20	5 hrs.
Perille oil	15	75 min.
Crude soybean oil	15	75 min.
Rosin dissolved in alcohol	20	1 hr.
Diglycol dilevulinate	10 to 30	30 min.
Joyoba liquid wax	15	20 min.
Cottonseed oil	15	15 min.
Acrawax	30	15 min.
Japan dryer	7.5 to 30	10 min.
Turpentine	7.5 to 30	10 min.
Nonaethylene glycol monostearate	10 to 30	10 min.
Nonaethylene glycol hexaricinoleate	10 to 30	14 min.

* See page 60.

* N.B. Vinsol added to PVA treated soil: all others added to PVA solution before application, some as solution, some as emulsions. All the materials listed below linseed oil appear to have no merit. Sodium stearate and tung oil were the ones used most. Although it is not listed, stearic acid is a good water repellent, but stearic acid appears to decrease the film strength of PVA. (1, p. 19)

The attempt to insolubilize the dry films of polyvinyl alcohol covered the rest of the investigations. The investigations may be subdivided into the following sections:

a) Chromium Compounds. The effectiveness is negligible: wet strengths were of the order of ten per cent of the dry strength, except in cases where tung oil was also used, where wet strength was of the order of 25 to 30 per cent of the dry strength. (1, p. 17)

b) Sodium Silicate. This has absolutely no value when used with PVA.

c) Melmac S-77-W, supplied by the American Cyanamid Company. This is presumably trimethylol melamine, made by the reaction of formaldehyde with melamine (condensation product of three molecules of dicyanodiomide, the latter being made from calcium cyanamide). It is made to set from aqueous solution by acidification or long standing. The combination of Melmac and sodium stearate used to insolubilize the PVA gave good results. Note that this may not be usable with alkaline soils since acidity is required for curing Melmac. (1, p. 20)

d) Dimethylol Urea, Ethocel and Vinsol. Dimethylol Urea, supplied by E. I. du Pont de Nemours & Company, is a basic material from which urea-formaldehyde plastics and adhesives may be made. It is a condensation product of two molecules of formaldehyde with one molecule of urea. It sets by polymerization from a water solution: this may be hastened by lowering the pH.

"Ethocel lacquers presumably were chiefly concentrated solutions of polymerized ethyl cellulose dissolved in organic solvents." (1, p. 5) Insoluble in water, they are emulsifiable although with some difficulty. Ethocel has excellent adhesive and molding properties and a high compressive strength. They were supplied by the Dow Chemical Company.

"A large number of tests were made with Dimethylol urea in PVA solutions alone and in conjunction with other insolubilizers and water repellents." (1, p. 21) The best results were obtained when dimethylol urea was used in conjunction with stearic acid which served as an acidifying catalyst besides being a water-repellent. The behavior of DMU is similar to that of Melmac although larger quantities are required. It seems better to use the DMU in larger quantities, without the PVA. (Cf. Use of Urea-formaldehyde resins.)

Vinsol was good, but no better than sodium stearate. Finely powdered sodium and calcium resinate act as water repellents very much like Vinsol. Note, however, that tests carried out in humid atmospheres indicate that sodium stearate does not prevent the absorption of water vapor. "Although water repellents prevent the moistening of PVA binder by capillary rise, they do not prevent softening of the films by the absorption of water vapor." (1, p. 23)

An attempt to stabilize sand by pouring PVA solution met with the result that the solution, which rose to the surface of the sand to replace the water lost by evaporation carried with it the greater part of the PVA. It is obvious that setting by evaporation is bad. (1, p. 25)

Microscopic examination of PVA-treated sand indicates that the reason why only small quantities of PVA are required for stabilization is that tough adhesive films form about the points of contact of the soil grains. The most efficient use of PVA is obtained when the greater part of the adhesive is deposited in these contact areas. "Since the film is deposited where evaporation takes place, it is desirable to use a quantity of solution so small that very little capillary movement of the PVA occurs during drying." (1, p. 29)

Ethocel: Ethocel lacquers 536-3-1 containing 70 per cent solids, and 536-2-1 containing 60 per cent solids were tested. Results were not promising. Stabilization was not effected until the specimens had dried, and the wet strength was very low although ethyl cellulose is not soluble in water. A mixture with sodium silicate proved very good oven-dry. However, the percentages required were high all through. (1, p31)

Methylol Ureas and Melamine: Solidifying effectiveness of DMU and Melmac was investigated with a sand. It was necessary to increase the solubility of these stabilizers by partial resinification.

Melmac was poor at 0.5 per cent, but was remarkably good at concentrations of 4.0 per cent, cured by air-drying without acidification.

Dimethylol urea was very good, but air-dried specimens without acidification (catalyst) had very low wet strength.

Sesquimethylol urea showed poor wet strength. This may be due to insufficient curing time or too high pH.

Monomethylol urea appears to be quite inferior to the other two.

Finally it may be noted that Melmac, Weldwood, and DMU gave higher strength values than Portland cement, particularly under freezing conditions. (1, p. 36)

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SODIUM SILICATE

In 1925, a process of chemical soil solidification was invented by Dr. Hugo Joosten. The process was patented and came to be known as the Joosten Process. It consists of injecting sodium silicate into sandy subsoil strata, and immediately following this injection with the injection of a strong calcium chloride solution. "The resulting gel fills the voids in the soil and binds the grain particles together into a solid, permanent, sandstone-like mass of a hardness which increases with age. This mass is insoluble in water." (22, p. 849) Use of the process is recommended on any loose, not too fine, sandy soil, or layers of sand and gravel with a limit of clay content of 20 per cent, to depths not greater than 60 to 70 feet.

A subsequent patent claims, "According to my invention the masses to be solidified and the like are first impregnated with silicic acid containing salt solutions, alumina containing salt solutions or with other gel forming chemicals by forcing them into the mass, spraying them with the materials or treating them in any other suitable manner; whereupon gases, such as carbonic acid gas, are applied to the thus impregnated mass. By the subsequent introduction of the gases into the material to be solidified and previously impregnated with the silicic material, such as waterglass, a guarantee is given that the substances react upon one another in the manner required to form a silicic acid regulus or another gel in status nascendi so that the surface forces then developing exert a solidifying action." (6) Several advantages are listed for the use of gases rather than other soluble chemicals for precipitating the gel. Similarly Michael Muller claims, "The process of chemically solidifying earth, which consists in saturating the earth with silicic acid containing substances and then applying chlorine to it." (20) The process of employing gases for precipitating the gel is not so commonly used, however.

The injection technique commonly employed, where the second chemical used is a concentrated solution of a salt, is described in several articles. A definite order of injection must be observed. The sodium silicate solution is injected when the pipe is being driven down, and the concentrated saline solution is injected when the pipe is being pulled out. Injection pipes about $1\frac{1}{2}$ inches in diameter which are perforated at the lower couple of feet, are driven into sandy soil at intervals of a couple of feet. A stability is obtained according to the kind, fineness and quartz content of the sand. (17) The details of another injection procedure were patented by Mr. Lars R. Jorgensen. (8) Chemically, there is no modification of the Joosten process offered in this patent. (Information: Mr. L. R. Jorgensen, 90 El Camino Real, Berkeley, California.) Most suitable for treatment are siliceous deposits of ballast, gravel and sand: they may be water-logged or dry, and up to a certain point, clean or dirty. Clays, lime soils, muds, silt, and peat are unsuitable. (19, 21) Solidification may be considered unlimited: "the solidified body, as a rule, is lasting only under water or in the range of soil moisture." (17) The process is used mostly for the sealing of pervious foundations, which is achieved through filling the pores with the silica gel. "Since silicic acid is a stable compound and is able to offer resistance to acids and salts occurring in nature, and since the gel remains in a swelling condition through the moisture of the soil, thus a scientific foundation is given for the durability of the consolidation." (9, p. 987) Commercial grades of sodium silicate are used but mixed with certain other chemicals, and diluted to the required specific gravity. The strength and proportions of the chemicals are important, especially in controlling such factors as the time of gelling. (23, p. 222)

In practice, the Joosten process as outlined above presents several difficulties. As experience has been suggesting methods of overcoming these difficulties, these new ideas have been the subject of various patents. Some of these will be briefly mentioned below.

(1) Charles Langer claims that "according to this invention, one injects into such masses a single solution containing sodium silicate, acid and at least one soluble metallic salt in such proportions that a silicic acid gel will be formed after a controllable lapse of time. I have discovered that such control can be effected by varying the proportions of these ingredients." (10) The disadvantage of the use of a slow-acting weak coagulant is that it fails to bring about the desired solidifying action. It is claimed that by adjusting the pH of the solution to counteract the alkalinity of the soil, strong coagulants can be used. This general method is apparently called the K.L.M. process. It is claimed that a number of different metallic salts and acids are suitable. An example is given as a reagent consisting of copper sulphate ($CuSO_4$) and dilute hydrochloric acid (HCl), mixed with the sodium silicate. (27) (Information: Mr. Joseph D. Lewin, 500 Bedford Avenue, Brooklyn, N. Y.) Mr. Lewin states that the method is applicable to soils with a permeability range of 0.1 to 0.0001 cm. per second for water at 60°F. The viscosity of the silicate of soda should not be less than 42° Bé, and a sodium silicate of ratio $Na_2O:SiO_2$ of 1 to 3.22 is recommended. It is claimed that to prevent sudden congealing of silicate in the presence of salty soils,

sulphuric acid may be added. (13, pp. 61-62)

(2) Hugo Joosten states that methods proposed for simultaneous application of both chemicals involving the careful choice of concentration of sodium silicate and acid and/or precipitating salt solutions, so as to avoid immediate gelation, are not reliable and impair the strength of the solidified mass by dilution. (7) "It now has been found that the aforesaid drawbacks may be avoided but nevertheless the solidification of the masses may be attained by pressing in a single solution of chemicals when a concentrated solution containing the silicic acid solution in an unstable or labile state is applied. For this purpose a composition is specially suited which is formed from a concentrated solution of an alkali silicate by first adding a suitable precipitating metal salt solution, particularly such of soluble zinc salts, e.g., zinc chloride or sulfate, and then bringing the precipitate thus obtained again to solution by adding ammonia or substances containing ammonia." Escape of ammonia, which may be speeded by introducing other gases or vapors, induces complete precipitation of the gel. Further little modifications of this general idea are presented.

(3) Tore Gunnar Marlberg also discusses the disadvantages of the proposal to effect delayed precipitation of the gel by adding small quantities of calcium hydroxide or calcium chloride to the alkali silicate solution, or by the addition of very dilute acids. (16) "The invention is characterized by the fact that the injection is carried out with a single solution which is prepared from alkali silicates, such as water-glass, in admixture with substances which have a lowering action on the hydroxyl ion concentration of the solution without having any strong precipitating action on silicic acid, namely acid salts of weak acids, e.g., acid alkali or ammonium salts of carbonic acid, sulphurous acid, boric acid and oxalic acid, such as sodium bisulphite, $NaHSO_3$; sodium dekaborate, $Na_2B_{10}O_{16}$; acid potassium oxalate, KHC_2O_4; potassium tetra oxalate, $KHC_2O_4 \cdot H_2C_2O_4$; and others."

(4) William Bruce Lerch and collaborators claim "a method of plugging formations in wells which comprises the step of introducing into the formation to be plugged a liquid gel forming material comprising a mixture of one part sodium silicate diluted with one part water associated with an equal volume of a mixture of 3½ parts hydrochloric acid and 19 parts of a sodium bisulfate solution and allowing the mixture to solidify when in place to form a solid mass." (13)

(5) John J. Grebe claims the invention of a method of preventing infiltration in wells involving the use of mixture of a silicate solution and a water-soluble soap capable of

forming a water-insoluble precipitate with calcium and magnesium salts. (5) The advantages listed for the use of the water-soluble soap are not too closely related to the problem of soil solidification but perhaps the same general idea would serve to combat some of the difficulties of poor water-resistance mentioned below in connection with the use of sodium silicate for soil stabilization.

Further mention of the use of sodium-silicate in reactions fundamentally the same as that of the Joosten Process is made in the following articles:

(1) Snell and Farkas discuss quick-setting silicate-of-soda cements. (26, p. 525) Three kinds of cements are considered: (a) mixture of inert material (siliceous aggregate) with sodium silicate, hardening by slow drying (b) mixture of inert and acid material with sodium silicate, hardening both by drying and by a reaction which liberates silicic acid (c) mixture of inert and alkaline or neutral material with sodium silicate, which by reaction will produce an insoluble silicate to give a set preliminary to drying. A silicate of soda of $Na_2O:SiO_2$ ratio 1 to 3.86 is used. Any material added to the cement, which will react with the silicate to neutralize the alkali present and precipitate silicic acid, causes the cement to harden more quickly than drying out of the silicate solution. The addition agent is either an acid or one that gives an acid reaction in solution. Small additions of $CaSO_4$ or $PbCO_3$ or $Ca_3(PO_4)_2$ increase the rate of set. The silicic acid itself has no bonding power, but the cement so transformed in place has a very definite and satisfactory bonding strength.

(2) E. Lemaire subdivides the reactions involved in the fabrication of silicate cements into the same three classes mentioned above. (12, p. 502) For acid materials he mentions the common use of organic acids (oxalic, stearic, oleic) alone or in mixtures, and also reagents that form an acid in the presence of water (fluosilicates, fluostannates). For neutral or alkaline materials he mentions Al_2O_3, $Ca(OH)_2$, $Mg(OH)_2$, $Ca(NO_3)_2$, $CaCl_2$, $Ca(CH_3COO)_2$. He states that adherence increases with increase of speed of hardening in moist air, being maximum for reactions using acids; but too rapid a set destroys adherence. The reagent must be poured on to the silicate and not vice versa.

(3) K. Pohl states that the soils most effectively treated contain about 20 per cent silica sand, and that compressive strength increases with time attaining within six months about 200 per cent of the immediate value. (22, p. 14)

(4) L. Gershwind mentions the use of sodium silicate in building roads with calcarious aggregate. (4, p. 523) There is no gelling caused by the lime, but the silica sets by drying. He claims it is well known that the adhesive power of a silicate varies directly in relation to the relative richness of silica (SiO_2); the variation of this binding power is particularly great between $Na_2O:SiO_2$ of 1 to 2.9 and 1 to 3.9.

(5) R. Feret discusses the hardening of rocky material by sodium silicate solutions and comes to the conclusion that it appears due mostly to the precipitation, under certain influences of a silica gel. (3, p. 415)

(6) M. P. Deslandres presents the idea of impregnating poor calcarious stone with silicate of soda, and again emphasizes the absolute necessity of using ratios of $SiO_2:Na_2O$ greater than 2.6 to 1.0. (2, p. 220)

(7) The Road Research Laboratory, Great Britain, (1) summarized available information on the use of sodium silicate with calcarious aggregate.

(8) Finally, the Road Research Laboratory conducted some laboratory experiments in the use of sodium silicate as a stabilizing agent for low-grade limestone bases. (25) The following results are reported, using a silicate having a $Na_2O:SiO_2$ ratio 1 to 3.5.

(a) "A rapid increase in compressive strength takes place up to 21 days after the mixture has been compacted in humid curing. Beyond this time, little or no increase takes place up to 42 days."

(b) "The compressive strength of cube specimens increases with silicate content up to the limit studied, viz., 7.5 per cent. The strengths obtained are of the same order as would be expected if Portland cement had been used as a stabilizer."

(c) "The maximum compressive strength obtained (about 1000 psi.) for a given silicate content and period of curing was greatest when the limestone contained about four to ten per cent of material passing the #100 B.S. sieve."

(d) "A reduction in compressive strength of about 20 per cent is obtained if specimens of limestone treated with silicate are frozen at -5°C. for periods varying between one and eight days. If the freezing period is extended to 14 days the loss is about 70 per cent." "There is no evidence to determine whether the loss of strength due to freezing is permanent or whether the material would recover its strength if allowed to cure for a longer period."

The possibility of using sodium silicate in solidification of clays (not by injection) is indicated by a few articles. "Experiments with fuller's earth and a plastic fire clay, which were free of soluble salts and were saturated with hydrogen, indicated that base-exchange reactions may also cause hardening of silicate mixtures out of contact with air.* ~~Natural plastic and magnesium were present as exchangeable bases, but they did not harden when these bases were absent~~." (18, p. 170) This paved the way for investigations such as that on the use of silicate of soda as a soil stabilizing agent, in which the investigation was directed at the stabilization of clays. (11)

The preliminary investigations were carried out on pure clay minerals of the kaolinitic, illitic, and montmorillonitic types. Silicates used in preliminary tests had $Na_2O:SiO_2$ ratios of 1 to 3.2, 1 to 1.6, 1 to 2.00, 1 to 2.4, 1 to 2.9, 1 to 3.9, 1 to 1, 3 to 2. The latter six silicates were not studied farther either because they were impractical to use of because results were not promising. The results are summarized below, although it is felt that the original report leaves much open to question:

<u>Kaolinitic</u> <u>Materials</u>: "The resistance to crushing of kaolinite briquettes increased with increasing silicate concentration."

<u>Illitic</u> <u>Materials</u>: (1) Grundyite. There was an increase in strength with increasing silicate concentration. In general, this resistance to crushing increased when the grundyite-silicate mixture was aged in a saturated atmosphere before molding into briquettes.

(2) Illite. "The resistance to crushing of illite briquettes first incresed to a maximum and then decreased with increasing silicate concentration." Moist aging again was beneficial.

<u>Montmorillonitic</u> <u>Minerals</u>: The results were extremely variable. "There was no apparent difference between the response of calcium saturated bentonite and bentonite in its natural state." The natural bentonite apparently is a sodium saturated bentonite.

* Natural plastic fire clays, which contained negligible amounts of soluble salts, were found to harden out of contact with air when calcium and magnesium were present as exchangeable bases, but they did not harden when these bases were absent.

The second part of the investigations used certain representative soils. A technique was established for determining the nature of the action of the silicate. "It was found in the study of the clay minerals that each gram of SiO_2 (author's note: in the form of sodium silicate) added to quartz sand had an exchange capacity of 0.5 m.e. of ammonia. If the silicate of soda added to a soil is not chemically combined with the constituents of the soil, but is acting merely as a cementing agent it would be expected to increase the exchange capacity of that soil by 0.5 m.e. or less for each gram of SiO_2 added. If the increase in exchange capacity was significantly greater than this expected amount, it was evident that a chemical reaction had taken place between the silicate and clay mineral of the soil." (11, p. 12) On the basis of such a technique the authors claim that the silicate of soda reacted with Cecil Clay (kaolinitic), and Clermont silt loam; whereas with Wauseon Very Fine Sandy Loam, Brookston Silty Clay Loam, and Wooster Silt Loam, the effect was merely a physical cementation effect.

The research report presents two conclusions that are of value: (1) "All the data, both with soil and clay minerals, show that the silicate of high SiO_2 and low Na_2O content gave the most favorable results." (2) "One important conclusion to be drawn from the data is that it will not be possible to apply silicate of soda indiscriminately to all soil types and get favorable results." It is felt that the report is not very conclusive; if there is any reaction between silicate of soda and the clay minerals, full understanding of such a reaction is necessary prior to any investigation of solidification of clays by sodium silicate.

Finally, detailed mention must be made of a research report on a laboratory study of the effectiveness of various chemicals as soil stabilizing agents. (15, p. 2) "A thorough search of previous works on the subject of chemical soil stabilization indicated the possible use of several materials as effective stabilizing agents. The most promising of these appeared to be: calcium chloride, sodium silicate, silica gel, and other gelatinous substances such as the hydroxides of aluminum, iron, magnesium, and calcium." "The results of early studies indicated that sodium silicate was the outstanding bonding agent of the group." The work described in that report is hereby presented under the following headings.

Bonding Action of Sodium Silicate: (15) "It was clearly indicated by early testing that the sodium silicate method of treatment was far more effective with sandy soils than with those in which silt and clay predominated." The percentage treatment required for optimum strength increased, and the maximum strength attainable decreased with an increase in soil fines. In silts and clays it was difficult to obtain good dispersion of the silicate, in spite of the use of commercial wetting agents. Tests were conducted to determine the relationship between compressive strength and the amount of moisture in the sample after a period of curing. The "results indicate that the range of moisture content between 35 per cent and 30 per cent of that at which the specimens were compacted is critical, with maximum strength being reached when the samples have dried back to about 31 per cent of their molded moisture content." (15, p. 4)

Effect of Waterproofing agents with Sodium Silicate: (15) Since specimens treated with sodium silicate disintegrated with 24 hours of soaking in water, various waterproofing agents were tried. (For a table of these see the original report, 15, p. 13) Those showing some success were: fatty acids (oleic acid, cottonseed pitch); liquid asphalt and pitches; pickle liquor; lignin sulfonic acid.

The report states, "the most promising materials, however, were the aqueous solutions of the following salts; calcium chloride, magnesium chloride, barium chloride, aluminum chloride, magnesium sulfate, magnesium oxychloride, zinc silicofluoride and magnesium silicofluoride." These being all salts of polyvalent metal ions, it can be seen that reactions similar to those of the Joosten Process take place.

"With the exception of calcium chloride, all of the agents employed in this test resulted in lower dry strength values than were obtained for the 'control' specimens treated with sodium silicate only." (15, p. 5) The dry strength of treated specimens varied with the concentration of the calcium chloride solution employed; use of 30 per cent concentrations gave strengths as high as those of control specimens. The addition of ten per cent solution of sulfuric acid increased water resistance, but lowered the dry strength and developed a fine network of fractures in the specimens on air-drying. The addition of a two per cent NaCl solution to the calcium chloride improved the strength values somewhat.

Sodium-silicate with Sodium-aluminate: (15, p. 6) Separate application of the chemicals was tried: the specimens treated with silicate had to be allowed to dry back to maximum strength before being immersed in the aluminate solution for waterproofing. Optimum results were obtained (for eight per cent silicate treatment with sand) with a 24 per cent aluminate solution, a concentration which was also very satisfactory from the standpoint of penetration into the specimens. It was determined that sodium-silicate specimens treated with sodium-aluminate alone (without further admixtures of $CaCl_2$, etc.) gave best results. The waterproofing was merely moderate.

Combined application of the two chemicals was tried. The main difficulty is the extremely rapid chemical reaction between the two reagents. The immediate gelling made mixing and molding difficult. "Acids were used to reduce the high alkalinity of the chemicals, thereby retarding the rate of reaction. However, unless a very small amount was used, the acid itself caused the formation of a precipitate when mixed with the solutions. The small amount that could be used was ineffective in reducing the rate of reaction between the sodium silicate and sodium aluminate." (15, p. 7) The optimum ratio of the chemicals appeared to be four per cent sodium silicate to two per cent sodium aluminate, based on the dry weight of the soil.

The report on the investigation concluded with the statement that "Unless some method of controlling the rate of 'set' can be developed, this method would be unsuited for practical application."

It is felt that the field of application of sodium silicate is yet far from covered. The results presented by various investigators must be analyzed in the light of their techniques of treating and preparing specimens. Such results cannot be interpreted as general.

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MISCELLANEOUS

A variety of stabilizing or solidifying treatments have been used in particular projects over the world. The success reported with any such treatment has not been great enough to warrant extrapolation of such localised practices to wider fields of application. In some cases, the treatments seem very promising and merely await further research for greatly widening their field of application. An attempt will be made to mention very lightly as many such stabilizing reagents as have been met with in the literature review. Many of the references cited are only of very indirect interest. Chemical treatments for impermeabilization and waterproofing are covered herein because of possible value in stabilization work.

(1) Tung Oil: This material seemed suitable for fine sandy loam. Drying previous to immersion is almost necessary; the stabilizing effectiveness is proportional to the percentage treatment. (30, p. 9)

(2) Linseed Oil: This oil is a stabilizing agent of the same general nature as tung oil, but less effective. (30, p. 9)

(3) Cottonseed Oil: Results with a fine sandy loam were mediocre. (30, p. 10)

(4) Aluminum Stearate with Petroleum Oil (SAE 30): The dry strength was fairly good with a fine sandy loam. The aluminum stearate imparted some water resistance. (30, p. 10)

(5) Castor Oil: Castor oil proved unsuccessful in stabilization of a fine sandy loam. (30, p. 10)

(6) Rubber Latex: A 30 per cent rubber latex suspension with a one per cent ammonium hydroxide was used with a fine sandy loam in laboratory investigations which were fairly promising. The best results were obtained with a seven per cent treatment. The investigators believe that the use of a cold vulcanizing agent with the rubber latex will prove very advantageous. (30, p. 10)

The use of rubber latex for solidification was patented by E. A. Murphy (Dunlop Rubber) (32). A finely divided rubber composition is formed by precipitating from an aqueous rubber dispersion and is mixed with finely divided rock in the proportion of about 7 to 95 parts, and the mixture is compacted.

Another patent (8) claims that a plastic composition which may be used for building roads or road surfaces consists of a concentrated aqueous dispersion of natural or synthetic rubber and a quantity of Portland cement, or the like, at least sufficient to cause the dispersion to set or gel irreversibly. Similarly a British patent (43) refers to a quick setting mix for use in the construction of roads, comprising of a hydraulic cement, an aqueous emulsion of rubber and a gelling agent for the rubber emulsion to accelerate the setting of the mix.

Rubber latex may be used to plug up porous strata in wells. (19) In an earth formation containing an alkaline earth metal salt brine, the rubber latex is introduced into the formation through the well bore. Upon contacting the brine the latex is coagulated, thus forming a plug of rubber coagulum.

While some of these articles do not directly mention soil stabilization, it is evident that the ideas presented might well be put to such use.

In 1936, H. Barron reviewed modern practice in the use of cement and latex mixtures in the production of road surfacings. (3)

(7) Plasticised Sulphur: Plasticised sulphur is a product of the reaction between sulphur and organic sulphides, polysulphides, and polymers thereof. It has been successfully used for a brick road, as is reported by W. C. Rueckel and W. W. Deucker. (38) Plasticised sulphur is inherently strong, flexible, and resilient; it is resistant to attack by acids and H_2S, lubricating oils or petrol, and is unaffected by relatively high temperatures. The product is, however, vulmerable to attack by animal fats and oils, and certain soil bacteria. Its application presents some difficulty as it must be applied as a liquid and allowed to harden. It decomposes at 320°F.

W. W. Duecker also discusses the use of sulphur-sand cements. (13) The optimum ratio that can be used is 40 sulphur to 60 sand. Additives to sulphur such as Thiokol or carbon black to reduce surface tension and increase wetting power are employed. Apparently, the sulphur must be applied in its molten state.

Porous earth materials are solidified by a special process. (1) Molten sulphur is introduced into the area to be solidified and suction is maintained at different locations bounding the area so that diffusion of the molten sulphur is considerably facilitated.

Charles S. Ackley has made an improvement on the above invention for use in areas where the earth materials contain excess moisture. (2) Heat treatment is used to change the moisture to steam. A charge of an ignitable mixture of finely divided aluminum and iron oxide is used. Suction is established at one or more points removed from the center of heat and thus the steam is drawn off. The earth materials are then ready for solidification by the introduction of a molten bonding medium.

(8) Molasses: Molasses has been used with water or slaked lime on Indian roads. (16) Mention is also made of the use of molasses with lime for stabilization in China. (23) Molasses has a great hygroscopic property to keep moist and an adhesive quality to act as a good binder; the chemical action of lime with molasses produces tricalcium sucrate which is insoluble in water and therefore is not washed out by rain.

A study of soil stabilization with molasses was conducted in India. (52) The study was confined to clay soil. Additions of molasses up to five per cent to sand-clay mixtures containing 30 to 40 per cent of clay also proved highly effective. A nearly linear relation was shown to exist between the properties of molasses and the cohesive strength of the mixture. Incorporation of lime converted the sugars into insoluble saccharates which remianed diffused throughout the mixture and produced uniform hardening. A "recuperation" test showed that soil-sand mixtures stabilized with molasses could be broken-up and remoulded three times in a month without appreciable loss of cohesion, and a field test showed that a damaged surface could be repaired simply by wetting the material and reshaping.

A few other articles (33, 37) mention the use of molasses.

(9) Mineral Oil: A method of preventing landslides, due to water absorption by underground bentonitic strata, is to inject into such strata a low viscosity (between 50-500 seconds Saybolt Universal at 100°F.) mineral oil containing a small amount of oleophilic surface cation active wetting agent. (14)

(10) Sodium Carbonate: It is stated in a report on soil research that the progressive increase in cohesion in sand-clay mixtures containing increasing proportions of clay was noticeably intensified by the addition of a small proportion of sodium carbonate. (52)

K. E. L. Pennell (34) mentions the stabilization of earth roads with sodium carbonate.

(11) Calcium Carbonate: Leonard S. Copelin claims that soil in wells and other shafts can be solidified by the injection of calcium carbonate in the interstices of caving or loose portions. Waste or refuse lime, a by-product of the manufacture of sugar, is used. (12)

(12) Ferrous Sulphate: The effectiveness of ferrous sulphate alone as a stabilizing agent has been investigated with no success.

(13) Naphthalene Vapor: Naphthalene vapor is used by John C. Swan to solidify water-bearing strata in well shafts. (42) Natural gas heated to a sufficient temperature to keep the naphthalene in vapor form is used as a carrier.

(14) Magnesium and Corrosive Agents: Leonard C. Chamberlain claims a method~~s~~ of producing a sealing deposit in a well bore. (11) This is done by placing a mass of magnesium in the well bore, compressing it, and then adding a corrosive solution, such as ammonium chloride, which forms a water-insoluble corrosion product upon reacting with the magnesium.

(15) Paraffine: Mathais Garvey uses paraffine to stop veins leading to drill holes. (15) A cartridge of paraffine is dropped down the drill hole and then pressure up to 5,000 pounds the square inch is applied. This pressure forces the paraffine into the vein, thus stopping the leak and making it possible to resume drilling immediately.

(16) Anionic and Cationic Detergents: Water-soluble industrial detergents, cetyl pyridinium bromide and sodium alkyl sulphate, were investigated for use as water repellents on a fine sandy loam. (50) "The detergents used were unrefined samples of two industrial products." The sodium alkyl sulphate is an anionic detergent because when "dissolved" in water it gives rise to a metal cation and a complex organic anion in the same way as common soap, (sodium palmitate):

$$R\text{-}O\text{-}SO_2\text{-}ONa \rightleftarrows Na^+ + R\text{-}O\text{-}SO_2\text{-}O^-$$

The cetyl pyridinium bromide, a halogen salt of a quartenary pyridinium base, is a cationic detergent because when dissolved in water it gives rise to a complex organic action and an inorganic halogen ion in the same way as aniline hydrochloride:

$$C_{16}H_{35}\text{-}C_5H_5N\text{-}Br \rightleftarrows C_{16}H_{35}\text{-}C_5H_5\text{-}N^+ + Br^-$$

(50, p. 2)

Both detergents caused a surface tension reduction of about 40 dynes/cm. Sodium alkyl sulphate did not affect the heat of wetting of the soil, but the cetyl pyridinium bromide reduced it very markedly (30%). (50, pp. 4,5)

With the particular soil used the cetyl pyridinium bromide was as effective in water absorption tests as Vinsol and gum rosin: the sodium alkyl sulphate was ineffective. It is inferred from the data that the waterproofing effect of cetyl pyridinium bromide is due to the adsorption of the chemical on to the surfaces of the soil particles. Even at 0.1 per cent treatment there does not appear to be any increase in water absorption over that obtained with higher percentages. (50, pp. 1, 3) "It is known that cetyl pyridinium bromide is adsorbed from its aqueous solutions on to silica surfaces." "That such an effect occurs in soil is indicated by the fact that the heat of wetting of the soil is reduced by 30 per cent when it has been treated with the chemical. (50, p. 5)

In another investigation the waterproofing action of two cationic detergents (cetyl pyridinium bromide and cetyl trimethyl ammonium bromide) when mixed with an alkaline sandy loam was studied, but no waterproofing effect was obtained with this soil, which had a pH value of 7.3. This was attributed to the slight alkalinity of the soil. (55)

Anionic detergents, however, are probably effective for such alkaline soils. Tests were carried out with an anionic detergent (a commercial mixture of sodium stearate and palmitate) on chalk, selected as an extreme example of an alkaline soil. Small amounts (0.1%) of the detergent restricted the amount of water absorbed to that which the soil could take up without swelling. "The inhibition of swelling is an indication that the surfaces of the finer chalk particles are saturated with adsorbed anions even at low concentrations, so that their affinity for water is reduced." Larger quantities (up to 1.0%) reduced considerably the amount of water absorbed by the chalk. This subsequent decrease in absorption may be due to the blocking of pores in the larger (silt-and sand-size) particles of chalk. (55, pp. 1,4)

(17) Hydrofluoric Acid: Hydrofluoric acid is suggested for use in solidifying earth containing silica and quartz. (48) It is claimed that the hydrofluoric acid dissolves silica, forming silicon fluorite; earth salts and acids act to reprecipitate silica in statu nascendi thus achieving good cementation.

(18) Water can be excluded from sands in a gas or oil well by the use of soap. (9) The solution of soap is permitted to flow into both oil and salt water bearing sands. The soap, on contact with the salt water, plugs the pores of only the salt water sand and the oil flows freely. This prevents further entrance of salt water into the well.

(19) Another method for excluding water from an oil well penetrating both oil and water formations is given. (29) A solution of a cellulose material adapted to deposit out as an insoluble precipitate when diluted with water is used and pressure is maintained while the water is in contact with the material to cause deposition. The pressure is maintained for approximately a day and then released allowing the well to flow. "It is found that the water flow is substantially shut off while the oil flow is unaffected."

(20) Mention is made of an investigation on the use of a soil stabilizing oil supplied by Messrs. Shell. (54) It was recommended that one per cent hydrated lime be added to the soil in conjunction with the S.S.O. This soil stabilizing oil was a more effective water repellent than a 40 secs. viscosity "A" type tar; at about 14 per cent treatment these were as effective as Vinsol, but at low percentage treatments Vinsol is much more effective.

(21) Calcium Hydroxide: The conclusions of an investigation of chemical treatment of chert-gravels for use in base-course construction (48) are mainly: (a) The behavior as base courses of chert-gravels can be greatly improved by the addition of a basic material such as calcium hydroxide or granulated slag. (b) The basic admixture will be more beneficial if it is in a finely-divided state, unless it is also added to improve gradation.

Calcium hydroxide is also mentioned in the preparation of a synthetic stone. (51) Shale or other aluminosilicate material is incorporated with slaked calcium hydroxide and molded. The reaction product is probably a calcium aluminosilicate.

(22) A process for plugging formations in oil and gas wells is given by W. B. Lerch, T. M. White and E. J. Gatchell. (27) Their method is to introduce into the formation a liquid composition which consists of a mixture of unsaturated animal oil diluted with a saturated hydrocarbon and heavy organic solvent added to sulphur monochloride and allowing it to solidify. This forms a plug resinous in nature.

(23) The use of gypsum, with additions to control setting characteristics, for sealing earth formations is the subject of patents by Hermann Mehner (31) and Arthur C. Hamilton. (17, 18) Mehner employs minerals which become liquid by losing water of hydration on being heated, and which can be made to set by depressing the temperature. He cites gypsum as an example and claims there are advantages in using it in mixture with magnesium chloride. For sealing off porous sections in an opening in the earth, Hamilton uses calcined

gypsum and a retarder of a nitrogenous organic material with which the time of set can be regulated. (17) Some technical improvements relating to control of time of setting are claimed in a subsequent patent.

(24) Trass (a light colored volcanic tuff used in cement making in Germany) and lime are used as binder in trass-macadam roads. (6,7)

(25) Chemical methods of shutting off water in oil and gas wells are given by H. T. Kennedy. (21) Several materials form voluminous precipitates on contact with water. Antimony trichloride gives antimony oxychlorides; this material may be injected either in a concentrated water solution or dissolved in oil. Silicon tetrachloride forms a voluminous precipitate of silicic acid on contact with water. This precipitate forms an effective cementing material. Silicon tetrachloride is injected as an oil solution. Superfatted soaps and finely divided cements made up in aqueous suspensions are also mentioned.

(26) G. D. Rodio described the use of the "Rodio gel" for solidifying deep foundations. (39) Rodio gel, a product of the basic reaction of a calcium compound is used by injection. The two necessary ingredients, A and B, are mixed and the resultant, slightly viscous, completely homogeneous fluid is injected. The time of start and time of setting can be controlled.

(27) H. Joosten discusses the subject of impermeabilization. (20) Besides mentioning the Joosten Chemical Consolidation Method, and the Shellperm method, reference is made to the use of lime, sawdust, clay, mortar, and cement mixtures of varying degrees of thinness. Further, it is stated that in potash mining it has been necessary to use magnesite instead of cement because of the concrete-destroying action of various saline solutions. However, magnesite bodies (made of a mixture of burned magnesia and magnesium chloride lye) are not very durable either in water or in rock salt, calcium chloride, or magnesium chloride solutions.

(28) A British patent by A. D. Peterson (35) mentions the use of stone sand fillers and a non-volatile binding material.

(29) Another British patent (24) states that surfaces for roads, floors, and the like consist of metals in a fibrous or granulated condition and/or minerals and/or ores which do not readily dissolve in water mixed with a proportion of a dryer, pressed in situ and covered by a layer of heat retaining material so that the mixture is converted by an exothermic chemical reaction into a hard resilient material.

(30) In the Pacific, coral has been used in stabilization as an aggregate (35, 40) and also directly in soil solidification. (10)

(31) An American patent (23) claims a method of sealing strata in a well by injecting a liquid halogen compound of an element from either the silicon or titanium class into the strata and allowing it to react with water. In particular, petroleum solutions of silicon or titanium tetrachloride are mentioned.

(32) A patent by Bent, Loomis, and Lawton (4) states that soil can be consolidated by introducing an alcoholate of a metal which forms a water-insoluble hydroxide by reaction with water. Silicon esters are cited in the same connection.

(33) Another patent by Bent, Loomis, and Lawton (5) claims the decreace of permeability of a porous formation by introducing into the formation a treating solution capable of releasing fluosilicic ions and reacting this solution with a water-soluble alkali salt. A water-insoluble alkali fluosilicate is formed in the pores of the formation.

(34) A patent by Howard D. Lawton and Albert G. Loomis (26) proposes methods to overcome technical difficulties encountered in the use of the above process, in cases where the oil-bearing strata are contaminated with saline waters. In order to free the oil-bearing strata from such water, wetting agents and liquids in which both oil and water are highly soluble are employed.

(35) Harvey T. Kennedy (23) claims the same general idea of shutting off water from oil wells by use of chemicals that react with water to form insoluble solid matter. Salts of antimony, arsenic, bismuth, tin, and iron are mentioned (e.g., antimony trichloride). The use of a suspension of hydraulic cement in alcohol is cited.

(36) The process of sealing formations by introducing into the formation a deflocculated suspension of a comminuted material is described by Delmar H. Larson. (25) This suspension is of size and character that is non-colloidal, non-gelling, non-swelling, and capable of deflocculation when in a suspension and capable of ready sedimentation when the suspension is at rest. Barytes, iron oxide, strontium sulphate, ground limestone and the like when used with suitable deflocculating agents are given as examples.

(37) Gerrit Hendrik van Leeuwen has been granted four patents (44,45,46,47) in which he claims a process for impermeabilizing or consolidating ground and earth masses.

The process consists of supplying into the voids a hydrophilic colloid in the presence of solvating agents adapted to swell the same. The hydrophilic colloid is surrounded by a hydrophobic substance which inhibits the swelling of the hydrophilic colloid.

The process also uses an oleophilic colloid, the oleophilic colloid being surrounded during its introduction into the masses by an oleophobic substance.

Injecting simultaneously but separately into the masses a solution of colophony in solvent and a solution of an aluminum compound adapted to convert the acids in the colophony to aluminum salts, is given as an example of the process. The salts swell by absorbing the solvent in which the colophony is introduced.

The masses are impregnated with a suspension of swellable substance in a liquid carrier, the carrier being capable of acting as a solvating agent for said substance to swell the same upon contact. The swellable substance is surrounded during its introduction by a material which will inhibit the swelling action of the solvent. For example, "A water-bearing gravel layer is treated by simultaneously but separately injecting through pipes in the proportion 1:1 on the one hand a ten per cent colophony solution in a gasoline rich in aromatics, and on the other hand, a five per cent aqueous aluminum chloride solution. The acids contained in the colophony are connected into aluminum salts, which swell by absorbing gasoline." (47)

(38) A process for producing the swelling properties of a swelling bentonite clay in a non-swelling clay is the subject of another patent. (41) It is claimed that the addition of small amounts of tetrasodium pyrophosphate will change a non-swelling bentonite into a swelling bentonite suitable for plugging pervious strata.

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A DISCUSSION OF FUNDAMENTAL CONCEPTS OF COLLOID CHEMISTRY PERTAINING TO SOIL SOLIDIFICATION*

The term colloid does not refer to special substances like inorganic or organic chemical compounds, but to a state of matter wherein certain properties and phenomena are exhibited. Colloidal phenomena are mainly surface phenomena, or properties exhibited by matter when surface energies predominate. If the energy of a body is divided into two components - surface energy and mass or bulk energy - it is easy to see that surface energies predominate more and more as the ratio of surface to mass, or surface to volume, increases. It is well known that the smaller the size of a particle, the greater is the ratio of surface to volume, as may be noted in the following table:

Length of a Side	No. of Particles	Volume of Cube	Total Surface Area	$\frac{\text{Surface}}{\text{Volume}}$ cm^{-1}
1 cm.	1	1 cm^3	6 cm^2	6
1μ range of	10^{12}	1 cm^3	60,000 cm^2	60,000
$1 m\mu$ colloids	10^{21}	1 cm^3	60,000,000 cm^2	60,000,000

μ = micron = 10^{-3}mm. $1 m\mu = 10^{-6}$mm.

It stands to reason, therefore, that any solid body, upon reaching a sufficient degree of comminution, will exhibit behavior characteristic of colloids. Today it is the dimensional range between about 1000 and 20 $m\mu$ that is considered as the field of colloidal dimensions; this, of course, is arbitrary, and the boundaries are not distinct.

Colloidal systems that are most commonly discussed are suspensions of minute particles in an appropriate medium. Such systems are called disperse systems because they consist of individual particles scattered (dispersed) through a

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* The material for this section was acquired mostly from a study of the book "Colloidal Phenomena" by E. A. Hauser, McGraw-Hill Book Co. Inc., 1939, (1) and the article "Colloid Chemistry of Clays," by E. A. Hauser, Chemical Reviews, 37 287, (1945) (2) and also from notes taken by the author when attending courses on Colloid Chemistry given by Dr. E. A. Hauser at the Massachusetts Institute of Technology.

medium. A study of such disperse systems affords the easiest approach to an understanding of the fact that there is no sharp distinction between mechanical suspensions, colloidal dispersions, and true solutions. Civil Engineers are accustomed to the idea of an arbitrary classification of soils on the basis of particle-size. Arbritrary limits of particle-size have been set for the definition of sand, silt, and clay. If a silty clay is dispersed in a large quantity of water, we shall be dealing with a system which is at once a mechanical suspension, a colloidal dispersion, and also a true solution to the extent to which the silty clay contains soluble material. The separation proceeds on a basis of particle-size. The mechanically suspended particles, individually visible in a microscope, settle rapidly. The colloidal particles are not visible in an ordinary microscope but may be detected by means of an ultra-microscope. Dissolved matter is not even detectable by means of an ultra-microscope. It will be recognized, however, that although the subdivision on the basis of particle-size is somewhat arbitrary, certain very characteristic properties may be associated with any group. This is true of sands, silts, clays--and especially of particles in the colloidal range of dimensions.

At this point it may be well to spend a little time on essential terminology:

A sol is considered as the distribution of matter in a continuous medium, its individual particles being of colloidal dimensions; the individual particles are in vivid Brownian motion and the system will flow under the influence of a differential force - it has a zero yield point.

If a few grams of clay are shaken up in a liter of water, the resulting suspension of the colloidal clay fraction in water is called a clay sol. Since the dispersion medium is water, the suspension may rightly be called a clay hydrosol. The prefix attached to the word sol specifies the dispersion medium, as for example in the words lyosol (any liquid), organosol (organic liquid), hydrosol (water), aerosol (air), and so on. A dispersion of minute droplets of a liquid in another liquid, in which it is not miscible, forms an emulsion.

If a sol is rigid and does not flow under the influence of a differential force, but the rigidity of the solidified system is only due to a solidification of the dispersion medium, it is termed a solid sol. Considering again the case of a suspension of clay in water as an example, a solid sol is obtained if the water is frozen; the dispersed clay does not contribute in any way to the rigidity of the system. However, a colloidal suspension will frequently acquire rigidity without there being any solidification of the dispersion medium. Such a solid system composed of dispersion medium and colloidal disperse phase is termed a gel. The rigidity of the system is completely attributable to the dispersed colloidal particles; as will be explained later, this rigidity is believed to result from the particles being held in their position by the interaction of attraction and repulsion forces. The easiest way to visualize such a system in which the dispersed particles, and not the dispersion medium, are responsible for rigidity in the system, is to imagine that the particles touch each other at their extremities, forming a "house of cards" within which the fluid dispersion medium is occluded. This easy visualization has prompted the development of the "honey-comb theory of gel-formation (gelation)"; but, as will be mentioned later, there are serious objections to such a theory.

Flocculation is the formation of flocks, which are micro or macroscopically visible aggregates of colloidal particles. A flock is a loose, fluffy aggregation of individual colloidal particles; it will eventually settle out to form a loose precipitate. Coagulation is the process of decreasing the degree of dispersion, thus forming increasingly coarser suspensions. Single particles of a sol join firmly to form increasingly larger particle units which finally precipitate as coagula.

We distinguish between two major classes of colloids, but in this, also, it must be remembered that the distinction is not sharp but is based on a matter of degree.

(a) "If the colloid to be dispersed swells upon the addition of the dispersion medium or finally even loses its original coherence and goes into a colloidal solution (gelatin in water, or rubber in benzene, etc.) we speak of lyophilic sols in general, of hydrophilic or organophilic sols in particular." (1*, p. 27) (philic = loving) More recently the term lyocratic has been introduced for these cases on the assumption that such lyophilic sols owe their stability primarily to their affinity toward the dispersion medium. (krateo = control)

(b) On the other hand, we have lyophobic (phobos = fear) sols, wherein the disperse part exhibits no such affinity towards the dispersion medium. These sols may also be called electrocratic since the system owes its stability

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* These numbers refer to the references cited on page 91.

primarily to the electric charges of the individual dispersed particles.

1) Electrophoresis: If an external potential difference is applied to an electrocratic hydro- or aerosol, the suspended particles are made to migrate in the direction of that pole which carries a charge of opposite sign to that of the particles. This phenomenon, in which the suspended particles move in an attempt to balance the applied potential, is called electrophoresis. Considering the example of a clay sol (e.g., two grams of clay dispersed in 98 grams of water), if two electrodes are immersed in the sol and a potential difference is applied, the clay particles will be found to move to the positive electrode, since they carry a net negative charge.

2) Electrosmosis: In the above case, the particles were free to move; but in many cases the motion of the particles may be restrained or prohibited, for example, by placing a semi-permeable diaphragm in the way. In such cases, the liquid will move to balance the externally applied electric potential. This phenomenon is called electrosmosis (electro-osmosis, electroendosmosis, endosmosis). Clays at natural water contents are systems in which the clay particles are not free to move. Since the clay particles are negatively charged, the liquid surrounding the particles must have a net positive charge equivalent to the net negative charge of the particles, since the whole system is electrically neutral. On application of the external potential the liquid will therefore move to the negative pole in order to balance the potential. This phenomenon is being used for drainage of clayey soils with low permeabilities.

3) Fall Potential: If dispersed particles are forced to migrate through the dispersion medium without the external application of an electric potential difference, the very movement of the particles will build up an electric potential difference in the system. A common example is that of a powerful wind forcing dust particles to move rapidly through the air: the dust particles become charged, thus sometimes giving rise to dust explosions. This phenomenon is known as fall potential.

4) Streaming Potential or Flow Potential: It need hardly be pointed out that the important consideration in the above case is the relative motion of dispersed particles to dispersion medium. In the case of fall potential this relative motion is achieved by a migration of the dispersed particles in a stationary dispersion medium. If the solid phase is maintained stationary, and the dispersion medium is forced to move without external application of an electric

potential, the electric potential that results is called a streaming potential, or flow potential.

In order to explain these electrokinetic phenomena, the Guoy-Freundlich diffuse double-layer theory has been developed. The colloidal particle is electrically charged, and carries a layer of firmly attached liquid from the dispersion medium. We shall consider later, with special reference to the clay minerals, how these charges are acquired. This electric charge on the surface of a solid body is distributed in the plane of the surface, as it were, embedded therein. (Referring to Figure 1 in which a negatively charged particle is considered, this surface electric charge is represented by the "minus" signs adherring to the circumference that represents the boundary of the solid particle.) The whole system, dispersed particles surrounded by the dispersion medium, is electrically neutral.

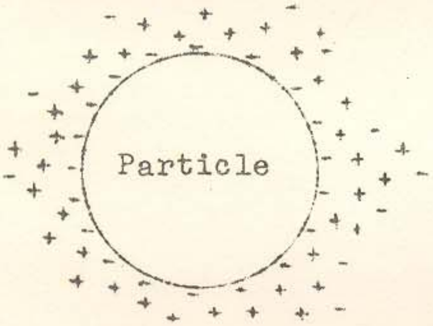

Fig. 1

Schematic presentation of the diffuse double-layer according to Guoy-Freundlich

The countercharges (represented by "plus" signs in Fig. 1) are located in the surrounding liquid in such a manner that the double layer of charges and countercharges extends over considerably more than monomolecular[1] dimensions into the liquid. The entire body of the dispersed particle surrounded by its diffuse double layer is called the colloidal micelle. The limit of the micelle is established as the point where the mean electric charge reaches a zero value. It has been stated above that the colloidal particle carries a layer of firmly attached liquid from the dispersion medium; however,

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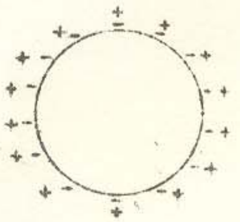
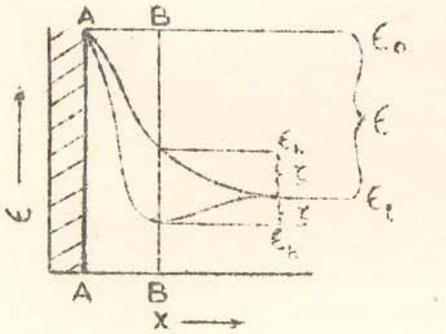
[1] The Helmholtz theory proposed a fully balanced double layer extending over monomolecular dimensions into the liquid. This theory helps to emphasize recognition of the fact that the system is electrically balanced, as shown in the accompanying schematic presentation. However, further mention of this theory is considered unnecessary, since it failed to be completely convincing and gave way to the Guoy-Freundlich theory.



the thickness of this layer is not necessarily, and is seldom, the same as the thickness of the entire double-layer. Thus commonly the part of the double-layer lying in the liquid is composed of two layers: the first part of the ions* and counterions lies in the firmly attached liquid layer, and the second in the freely movable liquid.

In electrokinetic phenomena the rigid liquid layer remains firmly attached to the solid particle, so that the liquid does not move against the solid interface, but against the liquid layer adhering to the interface. The thickness of the double-layer is abstract and depends on the surface charge present and on the concentration and valence of ions in the surrounding liquid; the thickness of the firmly attached layer may be considered in large part dependent on the hydration and valency of the ions embedded in the particle, if the charge on the particle is thus acquired.

The existence of charges and countercharges gives rise to a potential difference between the surface of the dispersed particles and the interior of the dispersion medium. We recognize, in general, the existence of two potentials: the <u>thermodynamic</u> (<u>galvanic</u>, ϵ) and the <u>electrokinetic</u> (zeta, ζ) <u>potential</u>. (Fig. 2) The galvanic potential is a



$$\epsilon = \epsilon_o - \epsilon_l$$

$$\zeta = \epsilon_h - \epsilon_l$$

A-A, boundary solid/liquid
B-B, boundary of attached liquid against free-moving liquid
ϵ_o, potential of solid surface
ϵ_l, potential of interior of liquid
ϵ_h, potential on the line B-B
A-B, firmly attached liquid layer
Cross-hatched area, solid wall

<u>Fig. 2</u> <u>Galvanic and Zeta Potential</u>

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* In this discussion the words "ions" and "charges" will be used interchangeably. It is assumed that the readers are aware of the fact that acids, bases, and salts will ionize to some extent when dissolved in water and that the ions are electrically charged: e.g., $NaCl \rightleftarrows Na^+ + Cl^-$; $AgNO_3 \rightleftarrows Ag^+ + NO_3^-$; $CaCl_2 \rightleftarrows Ca^{++} + 2Cl^-$. The valence of ions refers to the number of charges carried by the ion, e.g., calcium has a valence of 2, the calcium ion carries two positive charges. The hydration of ions is a measure of their affinity for water; the sodium ion has a great affinity for water and "firmly absorbs" a lot of water, i.e., is highly hydrated.

measure of the amount of charge embedded in the dispersed particles and is essentially independent of ion concentration and hydration except in cases where the charge of the particle is acquire through the preferential adsorption of ions. (See page 100) Depending on the number and disposition of the counterions, the curve of potential vs. distance from the surface of the particle takes on a definite shape: and the point where it crosses the imaginary boundary between the firmly attached liquid layer and the rest of the liquid, determines the magnitude of the electrokinetic potential. Note that the disposition of counterions surrounding the particle, their distance from the surface of the particle and their arrangement, depends on the strength of their electrostatic attraction and their hydration. Since in all electrokinetic phenomena the firmly attached liquid layer acts as if it were an integral part of the dispersed particle, it can be seen why the zeta potential is the only one directly controlling the behavior of the system in such phenomena (hence the name, electrokinetic potential). Consideration of the curves of potential vs. distance from particle (Fig. 2) will make it apparent that the electrokinetic potential depends on the galvanic potential: all other factors remaining constant, if the potential curves are started higher, corresponding to a higher particle charge, they will cross the boundary of the rigid liquid layer at a higher point. Similar considerations will lead to the conclusion that the zeta potential also depends on the thickness of the rigid liquid layer, the thickness of the entire double layer (determined as the point where there is zero net charge), and the type and number of counterions determining the shape of the potential curve. It may be noted here that it is quite possible for the zeta potential to have a different sign from the galvanic potential, if the potential curve goes through a minimum. (See Fig. 2) The zeta potential may also be zero (<u>isoelectric point</u>), although the galvanic potential still exhibits a finite value. Changes of zeta potential are brought about by addition of electrolytes: negative counterions, anions (Cl^-, NO_3^-, $SO_4^=$, etc.), influence a positive zeta potential in preference to cations (Na^+, Ca^{++}, Al^{+++}); and a negative zeta potential is primarily influenced by cations.* In the case of clays, for example, where the net particle charge is negative, the negative zeta potential is primarily influenced by cations.

The over-all effect of the active ion increases with its valency, since obviously the influence of an ion on an electric potential will increase with the charge associated

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* The influence of electrolytes on the zeta potential is discussed in greater detail on page 100

with the ion. Consideration of the effect of the hydration of the ion is being postponed; but for the present it will be stated that for assessing the influence of the active ion, the so-called "Hofmeister ionic series" is applicable:

$$SO_4 < F < NO_3 < Cl < Br < 1 < CNS < \text{----} OH$$

$$Li < Na; < K < Mg < Ca < Sr < Ba < Al < \text{----} H$$

Before considering these statements in greater detail it may be well for us to turn back to a consideration of the formation of the diffuse double layer. (Fig. 3) Considering for a moment the simple cubic lattice structure of silver bromide it becomes evident that whereas any atom in the interior of the cube is completely surrounded by a total of

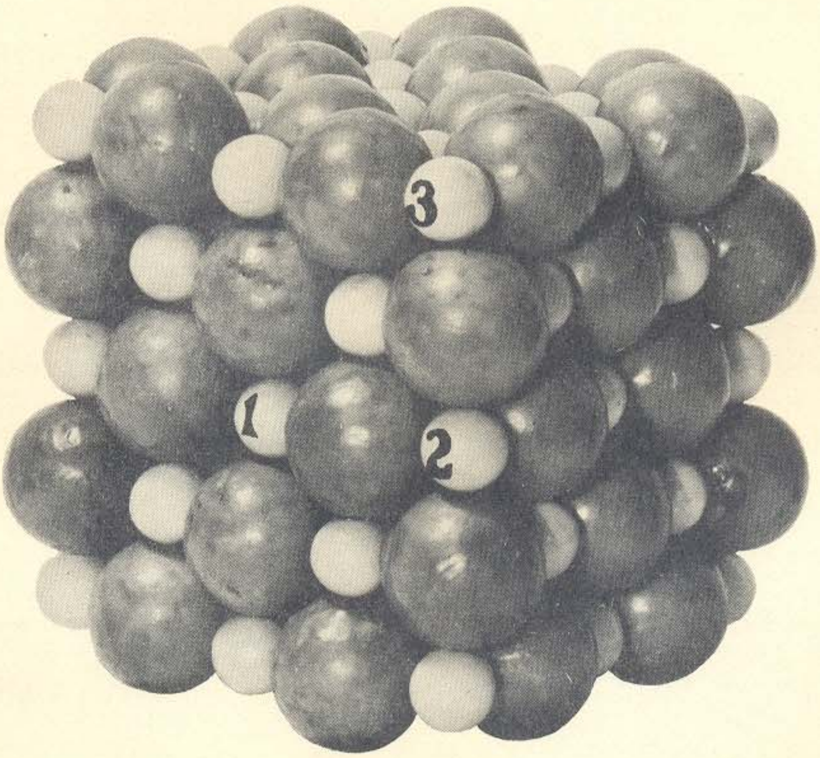


Fig. 3. Close-packed model of bromargyrite (AgBr) crystal. The silver atom, 1, is surrounded by five bromine atoms; only four are visible, the fifth being located behind the silver atom; silver atom, 2, is surrounded by four and silver atom, 3, by three bromine atoms (all are visible in the model). (From "Colloid Chemistry in Ceramics" by E. A. Hauser, American Ceramic Society Journal, 24 179, 1941)

six atoms of opposite ionic charge, atoms on the surface lack one such counteracting atom, atoms along edges lack two, and atoms at corners lack three atoms for completing saturation as shown in Fig. 3. It is such spots of surface unsaturation that offer opportunities for adsorption of ions, thus allowing the particle to acquire its charge (the charge that is considered embedded in the particle). It is logically observed that such adsorption of ions on surfaces should be a phenomenon of universal occurrence, and not restricted to particles of colloidal dimensions: this is true indeed, but these surface charges, or surface energies, are preponderant in determining the behavior of bodies only when the ratio of surface to mass is large--hence the very small size of particle that is commonly considered the range of colloidal dimensions. If the body increases in size other forces (such as gravitation) which depend on the mass become preponderant and the effects of surface energies, although present, are in proportion reduced to negligible status.

It may easily be demonstrated experimentally that if AgBr is produced as a precipitate of colloidal dimensions by the mixture of proper concentrations of NaBr and $AgNO_3$ solutions, the fine AgBr particles will be charged positively or negatively depending on there being present excess $AgNO_3$ or excess NaBr respectively. This experimental fact will serve as a suitable illustration of the fact that the adsorption of ions is preferential and follows very well defined laws. In the first case, we had an excess of Ag^+ and NO_3^- ions, and the colloidal AgBr particles became positively charged, which is evidence of the fact that Ag^+ ions were adsorbed in preference to NO_3^- ions. In the second case, an excess of Na^+ and Br^- ions led to a preferential adsorption of Br^- ions which resulted in negatively charged AgBr particles. Two main chemical laws are involved in this preferential selection of adsorbed ion: the Law of Least Free Energy and Fajans-Hahn Law which states that ions which can be incorporated into the lattice structure (i.e., ions of the same kind as already exist) are preferentially attracted. The adsorption of Ag^+ by the surface unsaturated Br^- is possible both because AgBr is insoluble (hence a system of least free energy) and because Ag^+ can fit into the lattice structure. (Fig. 4) The adsorption of NO_3^- ions by the surface unsaturated Ag^+ is not possible because that would result in the soluble product $AgNO_3$; and further, the NO_3^- ion does not fit into the AgBr lattice. On the other hand, similar considerations lead us to understand why in the presence of excess NaBr it is the Br^- ions, and not the Na^+ ions that are adsorbed, thus giving the AgBr particles a net negative charge. In this case, the Na^+ ions then form the counterions of the diffuse double layer.

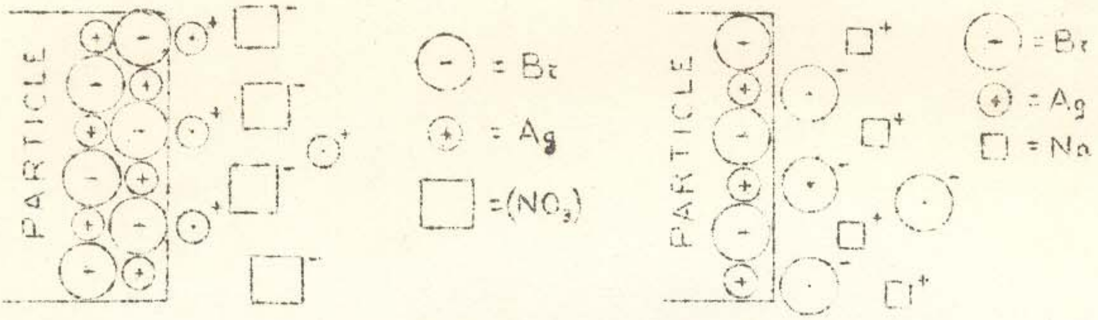
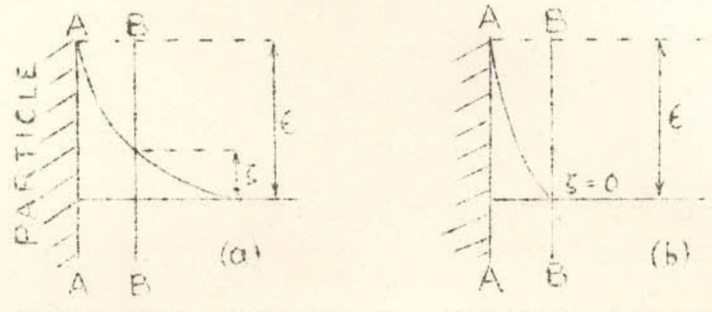


Figure 4

Schematic presentation of adsorbed ions, and counterions in cases (1) when there is an excess of $AgNO_3$ and (2) when there is an excess of NaBr.

In cases where the colloid acquires its charge by a process of preferential ion adsorption, as described above, the following changes are likely to take place on addition of excess electrolyte. First, up to a certain point which corresponds to a saturation of all the spots of surface unsaturation, increasing the number of excess ions available will tend to increase the zeta potential by increasing the galvanic potential (greater number of ions are adsorbed, the particle becomes more highly charged). An increase in zeta potential tends to increase the degree of dispersion, since the more highly charged "effective particles" will exert greater forces of repulsion on similar particles: such deflocculation may, for example, be achieved in the case of suspensions of kaolinite clay by addition of the proper small amount of electrolyte (sodium hydroxide). (Note: kaolinite acquires its negative charge by preferential adsorption of OH^- ions, because of the high dipolar configuration of the hydroxyl ion. This will be discussed in detail in the next section. At this point it is merely necessary to note that the charge on a kaolinite particle is acquired by preferential ion adsorption.) After all spots of surface unsaturation have been satisfied, however, further addition of electrolyte can merely cause a crowding-in of the counterions, thus decreasing the thickness of the diffuse double layer (since the point where the mean electric charge reaches a zero value will be closer to the solid particle surface). In other words, the crowding-in of counterions into the diffuse double layer, and especially into the firmly attached liquid layer, makes the potential curve steeper. If the decrease in double layer thickness reaches the point where the entire potential drop takes place in the liquid zone firmly attached to the particle, the zeta potential reaches a zero value (isoelectric point): the system is unstable and will tend to flocculate out, although the galvanic potential still exhibits a finite value. (Fig. 5) The higher the valency of the added ions, the stronger will be the influence that they exercise (Hardy-Schulze valency rule), since the valency of the ions reflects the number of electrical charges carried by them, and all the changes considered above are effected by the electrical charges of the ion. It must be noted that actual changes in the zeta potential are not as simple as outlined above since simultaneously the degree of hydration of the ions has effect on the zeta potential through modifications of the thickness of the firmly adsorbed water film, at the edge of which the zeta potential is measured.

Fig. 5



Changes of the Zeta Potential, the Galvanic Potential and the Thickness of the Rigid Liquid Layer Remaining Constant

(a) Zeta potential prior to the addition of electrolyte
(b) Zeta potential after addition of sufficient electrolyte
AB = thickness of firmly adsorbed liquid layer

The possibility of hydration of the surfaces and of the ions present cannot be disregarded. A thick layer of firmly adsorbed liquid will mechanically prohibit the dispersed particles from coming into contact. The stability of sols is, therefore, a result of both the electric charge of the particles and the non-compressibility of the hydrated shell. It has been pointed out above that there is no sharp demarcation between hydrophilic and hydrophobic sols. Hydrophilic sols, as a result of their affinity for water, acquire strongly adsorbed water hulls, and, as a rule, do not coagulate on losing their electric charge. Although they admittedly exhibit a minimum of stability at the isoelectric point, the addition of a suitable dehydrating agent (alcohol) is a necessary condition for their coagulation. To sum up, it may be stated that both the electric properties and the lyophilic (hydrophilic) properties play a deciding part in all phenomena leading to coagulation; and the distinction between lyophobic and lyophilic colloids is established on the basis of the predominating influence.

The phenomenon of surface dissociation is the basis of another process of formation of the diffuse double layer. For example, in dispersing sodium stearate (soap) in water, we find that the highly hydrated sodium ions having great affinity for water dissociate themselves from the nucleus and go into solution. (Fig. 6) This phenomenon closely

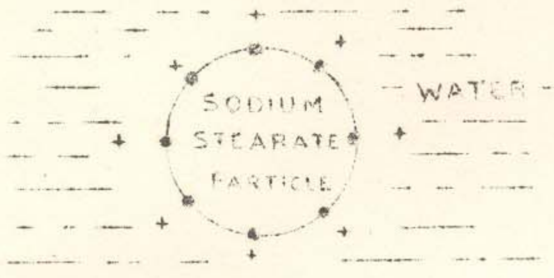


Fig. 6 Surface Dissociation

° Stearate ion⁻

+ Sodium ion

Copied from "Colloidal Phenomena" by E. A. Hauser

resembles the phenomenon of dissociation or ionization of electrolytes ($NaCl \rightleftharpoons Na^+ + Cl^-$) since, for example, sodium stearate when dispersed in water gives rise to a complex organic anion and a metal cation:

$$Na\ (\text{Stearate}) \rightleftharpoons Na^+ + (\text{Stearic acid ion})^-$$

However, the large and complex organic ions have no affinity for water, whereas the sodium ions have a great affinity for water. As a result, the complex organic ions form the nucleus of the micelle, and the sodium ions form the counter-ions of the diffuse double layer. The example of a soap given above resulted in a negatively charged nucleus by surface dissociation upon dispersion in water. (For a discussion of this phenomenon in relation to the colloid chemistry of clay minerals refer to the discussion of montmorillinitic clays, page 117) The case of a positively charged nucleus is quite as common, as for example in the case of a dispersion of cetyl pyridinium bromide in water:

$$C_{16}H_{35} - C_5H_5N - Br \rightleftharpoons C_{16}H_{35} - C_5H_5 - N^+ - Br^-.$$

It seems that the Hardy-Harkins rule of least abrupt change in a system holds, determining which ion splits off to form the counterion.

As has been stated in connection with the definition of a gel, the fact that the rigidity of the system is completely attributable to the dispersed particles has brought forth the theory that the dispersed particles (usually highly anisometric) touch each other at their extremities, forming a strong skeleton like a "house of cards." There is considerable experimental evidence to indicate, however, that many gels are formed when it is virtually impossible for the dispersed particles to be sterically connected. A more generally accepted theory of gelation considers the rigidity of the dispersed phase to be due to the interaction of attraction and repulsion forces between the sterically independent dispersed particles in the colloidal system. Another phenomenon which is explained by similar considerations is the phenomenon of isothermal sol-gel transformation, thixotropy; thixotropic gels revert to sols on shaking, and on standing regain their original rigidity. Attention will here be given to a discussion of some of the attraction and repulsion forces at play in such colloidal systems.

The concept of the existence of attraction and repulsion forces between molecules is quite generally accepted. The assumption of a force of attraction between the individual constituents of a liquid or a solid is necessary for the explanation of the tensile strength exhibited by solids and liquids, and, on the other hand, the existence of a repelling force between particles is necessary for the explanation of the fact that the compression of matter requires energy. Such intermolecular forces may be represented as shown below, in Figure 7, where curves are drawn of intermolecular attraction and repulsion forces, and their resultant, as a function of the distance between the particles of a coherent system. These curves of forces as functions of distance may easily be transferred to an energy scale, and will, therefore, be called potential curves.

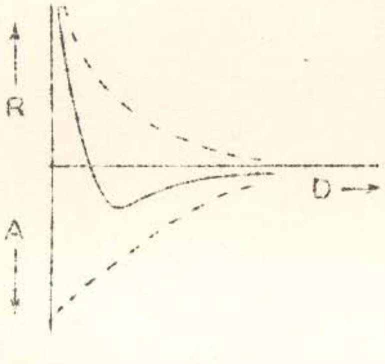


Fig. 7 Intermolecular Forces

A = attraction
R = repulsion
D = distance between particles of coherent systems

In colloidal systems, we can likewise obtain potential curves representing the energy of two particles plus their surrounding fluid as a function of the distance between such particles.* In the case of colloidal particles dispersed in water, or an electrolytic medium, the most important system

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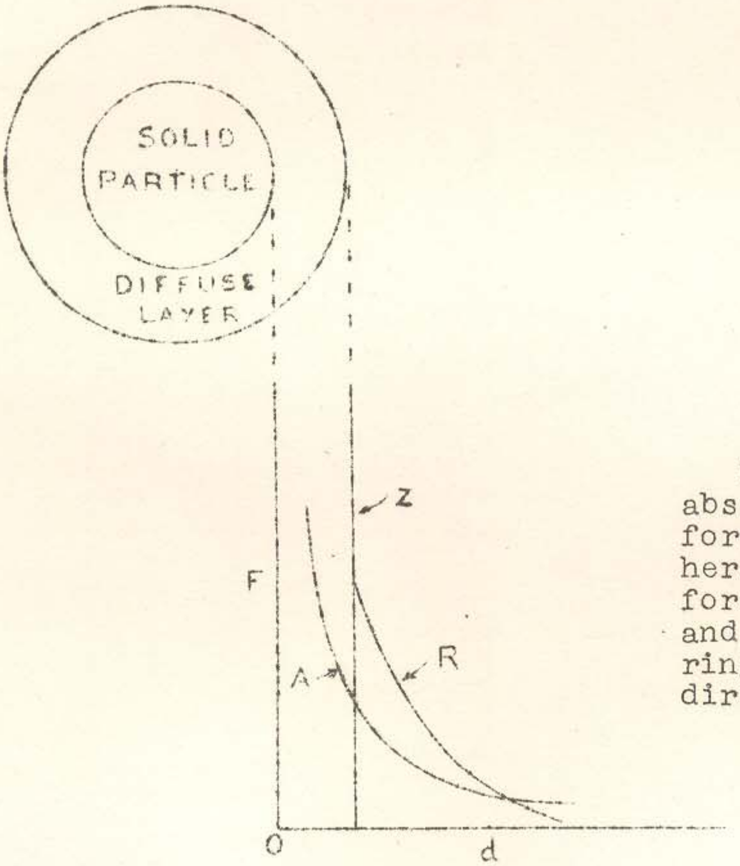
* For the original and detailed treatment of this subject, refer to C. Hamaker's articles: Rec. Tras. Chim. Pay-Bas 55, 1015 (1936); 56, 3, 727 (1937); 57, 61 (1938).

of attraction and repulsion forces are electrical forces arising from two sources. One set of forces arises from the ions which are rigidly bound to the surface of the particle, and the forces of opposite character are due to the counterions swarming around the particle. Inasmuch as the particles still carry a net charge, the number of counterions within the firmly adsorbed liquid layer must be insufficient for neutralization. The dispersion medium will carry a charge opposite to that of the colloidal micelle since some ions of opposite sign are randomly floating in it. Figure 8 gives an idea of the relative magnitude of the electrical forces associated with a colloidal micelle.



The axis F represents absolute magnitude of force. (No attempt is here made to represent forces of attraction and repulsion as occurring in opposite directions.)

Figure 8 "A schematic picture of the forces associated with the charge of a colloidal particle, the diffuse layer, and any given charge possessing the same sign as the particle, as a function of the distances separating them." Copied from "Colloid Chemistry of Clays" by E. A. Hauser, Chemical Reviews 37, 298 (1945)

"Line A represents the rate of decline of the electrical forces due to the basic charge of the particle with distance from the surface of the actual particle. Line R shows the decline of the electrical forces associated with the diffuse double layer of net opposite sign. The vertical axis Z intersecting A and R is the center from which all the counterions of the diffuse layer can be assumed to act." (2, p. 297) If the particle, as is the case with particles of colloidal clays, carries a net negative charge, then curve A would represent the force of attraction and curve R the force of repulsion for positive ions: the former being due to the negative charge, on the particle, and the latter due to the positive counterions assumed to act at a center of action as mentioned above. If attraction and repulsion act simultaneously, then a sum of the curves A and R would give a picture of the total-energy variation in the system, and it is this that controls the system's mechanics. The curves A and R can be considered as extreme cases of total potential curves. To realize the possibilities lying in between these extremes it is merely necessary to study systems where a curve of type R is gradually transferred into one of type A. (Figs. 9, 10, 11)

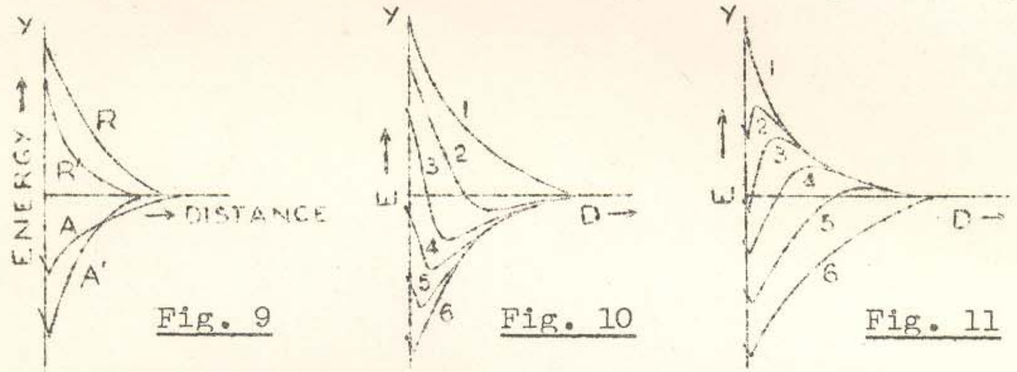


Fig. 9

Fig. 10

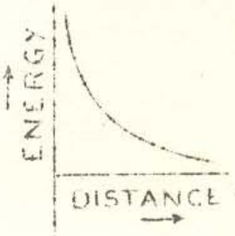
Fig. 11

Different Types of Energy-Potential Curves

A, A', attractive energy R, R', repulsive energy
Fig. 10 represents a set of intermediate curves when the attractive force is preponderant at large distances, the repulsion predominating when the particles are close together; Fig. 11 represents a set of curves wherein the resultant force is repulsive at large and attractive at short distances.

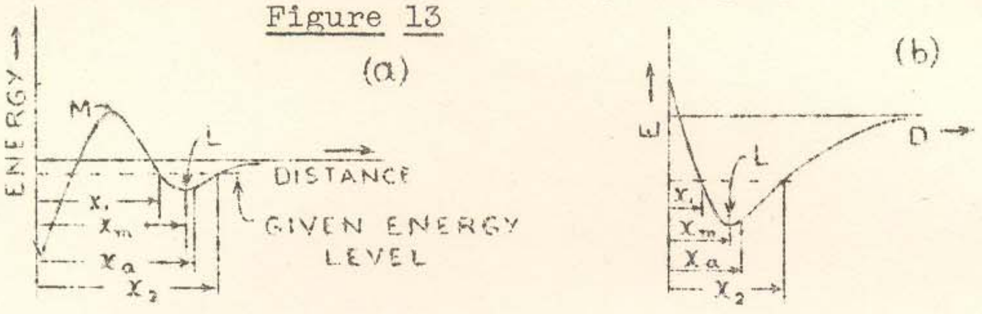
On the basis of these potential energy vs. distance curves, the behavior of the following systems may be explained.

A stable sol would be a system exhibiting energy-distance curves of the type shown in Fig. 12. Energy must be put into the system in order to make the dispersed particles approach one another. Note that systems which show a decrease in energy as the particles get together, will be unstable, and flocculate. Even in systems with energy curves such as shown in Fig. 13, if the



maximum point M is relatively low, the energy of Brownian motion, or agitation, or thermal energy, may be enough to push the particles over the hump M, bringing about coagulation.

Figure 13



A gel may be visualized as being a system with curves of the type shown above.(Fig. 13b, and perhaps even 13a) The existence of a pronounced minimum in the energy curve gives ample explanation for the phenomenon of gel formation. The theory that in gel and thixotropic-gel formation the dispersed particles acquire definite alignment and orientation (a theory that seems very plausible, especially in the case of highly anisometric particles, such as the plate-shaped clay mineral crystals), has been disproved by careful ultramicroscopic observation. The particles are merely held in place by counterbalancing attractive and repulsive forces: there being a pronounced minimum energy level, the system tends to settle to that level in accordance with the most fundamental natural law. Starting with the system at any given energy level some of the particles will be found at distances x_1 away from each other, while the remaining particles will be at distances x_2 from each other. On allowing the system to stand, the available fluid will tend to be homogeneously distributed throughout the whole mass, the distance between particles will be averaged out to x_{min}. Note that in general this can only take place when the trough is symmetrical about the Minimum Point L, assuming that one-half of the number of particles will be at each of the points x_1, x_2. However, even if we are dealing with a system where the average distance between particles is slightly higher than the minimum called for, we can still conceive of gel formation. The curious phenomenon of <u>synaeresis</u> takes place: in order to produce a system of minimum total energy a higher particle density must be achieved and hence a corresponding amount of fluid is expelled.

Systems which have the same type of energy curve as described above (Fig. 13a), with a high maximum M, but with a much less pronounced minimum L, would seem, according to the above theory, to represent systems exhibiting thixotropic behavior. By simple agitation (addition of kinetic energy) the gel easily changes to a sol: this sol reverts to the gel state upon standing.

Before finally dismissing this subject of the interplay of attractive and repulsive forces within colloidal systems, it may be well to point out that the plasticity of clay-water systems is considered the result of the attraction and repulsion forces set up between the colloidal clay micelles and the ions in the dispersion medium. It must be borne in mind that the above discussion, which merely considered the electrical forces of attraction and repulsion, was not meant to be exhaustive. In fairly dilute dispersions of clay in water, these electrical forces are the most important, and a consideration of merely these forces will give a fair picture of the system's mechanics. However, in lyophilic systems, or in the case of clay-water systems at low water-contents, admittedly the thickness of firmly adsorbed liquid layer is important; the mechanical action of the hydrated shell is equivalent to a force of repulsion preventing the dispersed particles from coming together. The same concepts of energy vs. distance curves may be used, but the energy curves will have to be drawn for the appropriate forces at play.

Two other phenomena which may be of interest in Soil Mechanics will here be mentioned in brief: they are the phenomena of rheopexy and dilatancy. With certain thixotropic gels the time of setting is enormously decreased if the system is subjected to gentle rhythmic motions such as tapping: this phenomenon is called rheopexy. "Whereas thixotropic systems have been obtained from all possible types of colloidal dispersions, truly rheopectic systems seem to be limited to laminar systems, for which the clays are perfect examples. Besides this, rheopectic clay systems are limited to those clays which also permit production of thixotropic systems. Whereas the setting up of a thixotropic gel does not call for any preferential alignment of the dispersed particles, ultramicroscopic studies of rheopectic systems indicate that the rhythmic motion applied to the sol orients and aligns the platy particles and thereby accelerates their taking up the equilibrium positions already referred to when discussing the phenomenon of thixotropy." (2, p. 311) In Soil Mechanics the phenomenon of dilatancy is often used as a means of ready identification of silts in their natural wet state. If a small pat of the wet material is placed on the palm of the hand and shaken, the surface becomes wet and shiny in appearance; however, if the pat is now compressed between the fingers, the water disappears from the surface leaving it dry and dull in appearance. In order that particles may form a dilatant system, it is necessary that they be absolutely independent from each other; dilatancy is destroyed if the particles show the least tendency to adhere to one another. The particles are usually at least as large as the upper limit of the colloidal range of particle-size, so that they are of sufficient size to permit sedimentation and tend to form closely packed sediments. Dilatancy has thus far only been observed with lyophobic systems. Civil engineers state that one of the requirements that a system must satisfy in order to be dilatant is that there be great mobility of the liquid within the pores formed by the particles; this requirement actually follows from the requirements outlined above. The following explanation of dilatancy was offered by H. Freundlich[*]: the external force causes an unequal distribution of the particles, which are piled up locally, thus forming cavities in other places which fill up with the free dispersion medium; when the external force is removed, the particles again repel each other and take up their original positions.

Having considered most of the fundamental colloidal phenomena that might be of interest in soil engineering, we may devote our attention to the one important reaction by means of which we may radically change the properties of colloid systems in general--and of colloidal clay systems, specifically. This is the ion-exchange reaction. In the case of those clay minerals which will in contact with water form a colloidal micelle, since the nucleus is invariably negatively charged and the surrounding counterions are cations, the ion-exchange reaction is a cation- or base-exchange reaction. The counterions of the clay particle can be exchanged with cations from the dispersion medium. Such exchange must follow the "law of least free energy", and, therefore, is only possible if the cations available for exchange in the dispersion medium would, by taking the place of the original counterions, result in a clay micelle with a lower charge or with a smaller tendency to hydrate, or both. Thus, for example, by adding calcium chloride to a dispersion of sodium-clay, we will obtain a calcium-clay by base-exchange of calcium ions for the sodium counterions. (Fig. 14)

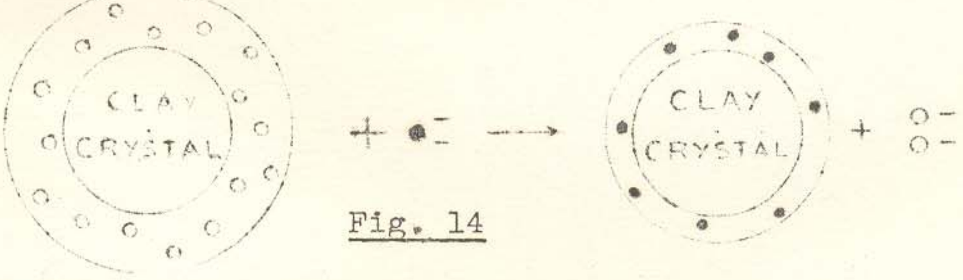


Fig. 14

○ Monovalent cation; e.g., Na^+ in the case of sodium-clay
● Divalent cation; e.g., Ca^{++}
- Monovalent anion; e.g., Cl^-

The specific reaction in the case of the example given may be written: $\boxed{\text{clay}}\begin{matrix}-\text{Na}\\-\text{Na}\end{matrix} + CaCl_2 \longrightarrow \boxed{\text{clay}}\,{}^{-}_{-}\text{Ca} + 2\ NaCl$

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[*] Trans. Faraday Soc., 34, 308 (1938)

Such a base-exchange reaction will obviously be more pronounced, the greater the number of highly hydrated exchangeable ions that the clay particle carries. The clay particle in Figure 14 is shown carrying sixteen sodium ions: it is, therefore, able to adsorb eight divalent calcium ions by base-exchange. The number of sodium ions that are actually associated with a particle of sodium-clay depends on the structural configuration of the clay crystal, as will be explained in the following section. Since the number of polyvalent cations that can be exchanged for the sodium ions of a sodium-clay depends on the number of sodium ions associated with the clay particle, it is evident that the number of polyvalent cations that can be exchanged will depend on the structural configuration of the clay crystal. It is difficult to find out the number of cations that can be adsorbed by each clay particle, and so the common measure used relates to the number of cations that are adsorbed per 100 grams of clay. This measure of the ability of a clay to adsorb cations is called the <u>base-exchange capacity</u>, which is expressed in milliequivalents of cations per 100 grams of clay.

"However, by the same reasoning, clays can also adsorb anions where net positive charges are set up in the crystal lattice, or where the hydrogen of a hydroxyl group is exchanged for a stronger ion, like PO_4^{---}. Quite generally one can state that ion exchange will follow the Hofmeister or lyotropic series, at least for cations, i.e., the higher the atomic weight of an ion, the more firmly it will be held by the exchanger. Therefore, the exchange reaction for monovalent ions will follow the series: $\mathrm{Li} < \mathrm{Na} < \mathrm{K} < \mathrm{NH_4} < \mathrm{Rb} < \mathrm{Cs}$, and for multivalent ions the series: $\mathrm{Mg} < \mathrm{Ca} < \mathrm{Sr} < \mathrm{Ba} < \mathrm{La}$.$^{++}$ In base-exchange of clays, however, the valency and hydration of the exchanging ion are not the only important considerations. The size of the exchanging ion is also important. Ions with an apparent diameter greater than 2.64 Å, which is the diameter of the circle one can inscribe into the hexagonal net of oxygen atoms forming the silica sheet of the clay-mineral lattice*, are held tightly on the silica sheet and are difficult to replace. Since the dry potassium ion has an apparent diameter of 2.66 Å we can understand why it is so difficult to replace, and why clays like mica are not readily affected by water. The size of the hydrated exchanged ion is, of course, of importance in influencing the thickness of the formed diffuse double layer, and it further controls the equilibrium exchange, as shown in Figure.15."(2, p.303).

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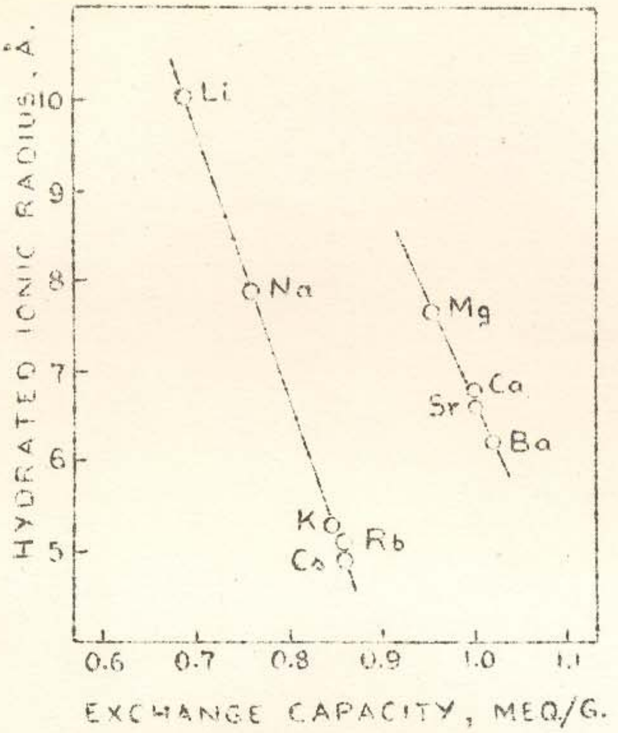
* This will be better understood after consideration of the lattice structure of the clay-minerals. The next section of this report attempts to present the important concepts for this study.

Fig. 15



Radii of hydrated ions versus exchange capacity at equilibrium (from "Colloid Chemistry of Clays" by E. A. Hauser, Chemical Reviews, 37,305 1945)

Finally, it must be mentioned that base-exchange is not, as was assumed for a long time, limited to inorganic cations. Complex organic cations can be introduced just as well, and it is such base-exchange that has afforded the greatest advances in the colloid chemistry of clays in recent years.

THE CLAY MINERALS

An understanding of the lattice structure of the main clay minerals is very useful towards an understanding of the behavior of clays.

In making this presentation* the writer wishes to emphasize that although some of the points still seem to be contradictory, he has felt that it is best to present a unified and clear picture that will serve as a rational basis for the explanation of the fundamental properties of clays. The lattice structures of the main clay minerals are presented as actual facts that have been fully ascertained. The points of controversy are not major: they merely involve little rearrangements. For the sake of clarity it may be better to present merely one consistent theory, fully realizing that it may in parts only be a working hypothesis, than to attempt to follow all the arguments for and against the various theories.

The most widely accepted theory is hereby presented.

For many years before the advent of the X-ray diffraction technique of studying the actual structural arrangement of the atoms comprising a crystal, chemical analysis was used in extensive studies to explain the differences in behavior of various clays. But the efforts were not successful, and it came to be realized that knowledge of the chemical composition of clays alone affords no sound basis for the prediction of the properties of a given clay. Besides the chemical composition, the spatial arrangement of the constituent atoms in relation to one another is of major importance in determining the properties of clays. Further investigation into the nature of the clay minerals has since proceeded on a basis of lattice structure.

The easiest way to understand the clay minerals, their similarities and their differences, is to visualize them as being built up from the same basic building units, the differences being, at least in part, accounted for by differences in the combinations of the building units. It is

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* The material for this presentation was acquired in large part from a study of the articles: 1) "Colloid Chemistry of Clays" by E. A. Hauser, Chemical Reviews, 37, (1945); 2) "Modern Concepts of Clay Materials" by R. E. Grim, Journal of Geology, 50, (1942); 3) "Colloid Chemistry in Ceramics" by E. A. Hauser, American Ceramic Society Journal, 24, (1941), the figures are all taken from this article; 4) "Plasticity of Clays" by Hauser and Johnson, American Ceramic Society Journal, 25, (1942).

far from the purpose of this presentation to discuss the actual genesis of the various clay-mineral crystals; and it is not contended that at some early geologic time these building units occurred as such in nature, and that they subsequently got together to form the clay minerals.

Discussions of the lattice structures of clay minerals usually are initiated with the concept of the silicon tetrahedron, the aluminum octahedron, and the magnesium octahedron as being the three main basic building units. These three primary building units are shown schematically as Figures 1, 2, and 3, page 120. The silicon tetrahedron is highly unbalanced electrically, since the silicon atom shares a total of four electrons with neighboring atoms and the four attached oxygen atoms require a total of eight electrons for saturation. Similarly the aluminum and magnesium octahedra are highly unbalanced. This unbalance corresponds to chemical valences, which act to combine the building units into more complex, but electrically balanced, structural units. The primary structural unit thus formed by the silicon tetrahedron is the hydrated silica sheet. Similarly the aluminum and magnesium octahedra form the gibbsite and brucite sheets. These are schematically shown as Figures 4, 5, and 6, page 120. The silicon tetrahedron, magnesium octahedron, and aluminum octahedron, being highly unbalanced, do not exist as isolated materials in nature. The hydrated silica sheet and the minerals brucite and gibbsite are electrically balanced structures, existing in nature in isolated form. The formation of the brucite, gibbsite and hydrated silica sheets from the magnesium and aluminum octahedra and the silicon tetrahedron will not be discussed herein. The brucite, gibbsite and hydrated silica sheets will for purposes of this report be considered as the primary structural units which combine to form the main clay minerals, namely the kaolinitic, illitic, and montmorillonitic clay minerals.

The gibbsite and brucite sheets will not be discussed in detail in this report. It is apparent from Figures 5 and 6 (page 120) that the layer lattices are saturated except for the edge and corner points of the sheets. In the gibbsite sheet trivalent aluminum atoms are sandwiched between two hydroxyl sheets, whereas in the brucite sheet divalent magnesium atoms occupy the positions between the two hydroxyl sheets. Because of the fact that aluminum shares three electrons while magnesium shares only two, the neutral sheet of aluminum octahedra can only be obtained if one third of the places occupied by magnesium in the octahedra sheet remain vacant. This results in the gibbsite sheets being somewhat more open-textured than the brucite. A study of Figure 14, page 121, in conjunction with Figures 5 and 6, page 120, will make the above point clear.

The hydrated silica sheet will be given somewhat more detailed consideration because the relationship of the size of ion in connection with the base-exchange properties of certain clays is dependent on the geometric configuration of this sheet, as is mentioned on page 109. In a hydrated silica sheet several silicon-oxygen tetrahedra are combined by sharing the appropriate oxygen atoms. This sharing of oxygen atoms may be considered as the result of a condensation reaction; as the name implies, this reaction involves the splitting off of a molecule of water when two hydroxyl groups are combined. For example, two compounds R(OH) and R'(OH) may condense to form a compound R-O-R' as shown: $\text{R-O}\boxed{\text{H + HO}}\text{-R}' \rightarrow \text{R-O-R}' \quad H_2O$. Thus the combination of silicon-oxygen tetrahedra may be considered as a condensation of tetrahedra which have the vertex oxygens replaced by hydroxyl groups. If silicon tetrahedra are combined so that two always share one oxygen, a zig-zagging chainlike structure results. Two such chains may further combine by condensation to form a hexagonal network structure. Figure 15 shows such a symmetrical network structure; to avoid confusion only one plane is shown, namely, that marked A in Figure 4, page 121. It will be seen that the oxygen atoms in this plane form a hexagonal network. An enlarged drawing of one such hexagon, drawn more truly to scale, is shown in Figure 16, page 121. It can be seen from this figure that the hole formed by each hexagon of oxygen atoms in this plane has a diameter of 2.64 Ångstrom units, which is the diameter of the oxygen atom.

It has been stated earlier that the common clay minerals can be considered as built up from the hydrated silica, brucite, and gibbsite sheets. The reaction by which these structural units may be considered to have combined to form the clay minerals, is the condensation reaction discussed above. The discussion of the complicated lattice structures of the clay minerals, therefore, can now be undertaken with great simplicity. This discussion will be limited to the clay minerals which are of greatest interest to the civil engineer engaged in soil mechanics work; namely the kaolinitic, illitic, and montmorillonitic clay minerals.

In the kaolin group the mineral halloysite deserves mention, although it is of somewhat rare occurrence because of its relative instability toward elevated temperatures. This clay mineral consists of a complete gibbsite layer lying on a complete hydrated silica sheet as shown in Figure 7, page 120. The gibbsite and hydrated silica layers are held together by secondary forces which effect the weak bond of cohesion between the OH-OH groups facing each other. At elevated temperatures condensation takes place, and a lattice identical with that of kaolinite results. A comparison of Figures 7 and 8 will show that the kaolinite lattice can be obtained from the halloysite lattice by splitting off a molecule of water from each pair of hydroxyl groups that are shown connected on Figure 7. The gibbsite and hydrated silica sheets in kaolinite are rigidly connected by shared oxygen links. Consideration of the lattice of halloysite is of marked interest; the progression of steps, starting with the stacking of a gibbsite sheet over the hydrated silica sheet, leading through the formation of halloysite to the eventual production of kaolinite by condensation, epitomizes the idea of the building up of the clay minerals from a few basic structural units.

Kaolinite is composed of a hydrated silica sheet combined, by shared oxygen bonds, with a slightly distorted gibbsite layer. The structure is electrically neutral, or balanced, from the point of view of electron distribution, except for spots of unsaturation along the edges of the sheets. Since the kaolinite crystals are electrically balanced, any increase in the size of parcels in a direction perpendicular to the plane of the sheets must be the result of a stacking up of crystals held together by secondary forces. Since these secondary forces are very weak in comparison with primary forces, cleavage will be easy between planes joined only by secondary forces whereas fracture across primary bonds is difficult. This ease of cleavage along planes parallel to the sheets of the layer lattice accounts for the fact that kaolinite clay particles are plate-shaped. The same is true of montmorillonite and illite. Further, it follows that the ease of cleavage depends on the strength of the secondary bond holding the individual parcels together. The secondary forces holding together parcels of kaolinite are relatively strong forces acting between the hydroxyl groups of one sheet and the basal oxygens of the silica sheet in the parcel stacked above. As will be seen later, the secondary forces holding individual parcels of montmorillonite together are relatively weak attraction forces between opposing oxygen sheets. This fact offers one explanation of the fact that montmorillonite is capable of a higher degree of dispersion in water than is kaolinite. The importance of adsorbed, hydratable cations in providing means to overcome the secondary bonds between particles by dissociation on contact with water, must also be recognized.

The kaolinite particle is electrically balanced except for unsaturation along broken edges, and the charge on particles of colloidal dimensions is acquired by adsorption of ions. Kaolinite dispersed in absolutely pure water will not form a stable colloidal suspension, because the colloidal particles do not acquire a charge. This fact is worth emphasizing because it sharply differentiates kaolinite from montmorillonite, which acquires its charge by surface dissociation of adsorbed cations and, therefore, disperses in absolutely pure water. (Refer to page 117) It was pointed out in the previous chapter, in connection with the acquisition of charge by colloidal crystals of silver bromide, that adsorption of ions must be preferential. In the case of kaolinite, hydroxyl (OH) ions are preferentially adsorbed, and the kaolinite particle thus acquires a net negative charge of a magnitude depending on the number of adsorbed (OH) ions. These adsorbed (OH) ions form the charge that is considered embedded in the particle, and cations from the dispersion medium will immediately form the counterions of the diffuse double layer. These counterions, cations, are exchangeable, and the number of them available for base-exchange (as well as their valency) determines the base-exchange capacity of the kaolinite.

The base-exchange capacity of kaolinite is known to be very low, being about 3-15 milliequivalents per 100 grams of clay. Further, the base-exchange capacity of kaolinite has been shown to increase with decreasing particle size, whereas the exchange capacity of montmorillonite does not vary with particle size. These findings are fully in accord with the differences in structure of kaolinite and montmorillonite. Thus from one point of view, in comparison with montmorillonite, the exchange capacity of kaolinite is low because there are no replacements within the lattice to set up unbalanced charges (see page 116). From another point of view, the base-exchange capacity of natural kaolinites is low because of the comparatively large particles that result from the strong OH-O secondary bond between individual crystals stacked over each other. It thus seems logical to assume that the broken bonds of the silicon and aluminum layers explain the adsorption of negative charges, and specifically of (OH) ions. The adsorptive capacity of kaolinite seems to be limited to broken oxygen bonds and/or the hydrogen of hydroxyls at flake edges. However, further thought indicates that only a limited number of negative charges are adsorbed on these broken edges, because the silicon and aluminum atoms are embedded in cavities formed by the much larger oxygen and hydroxyl atoms. It is very probable that the adsorption of hydroxyl ions, if they are present in the dispersion medium, will take place on the basal oxygen sheet of the individual particle. This adsorption is preferential because of the dipolar configuration of the hydroxyl ion.[*]

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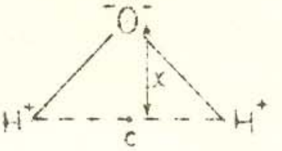
[*] A molecule in which the center of gravity of the negative charges does not coincide with the center of gravity of the positive charges has a dipolar configuration. Water, for instance, has a high dipole moment, $2ex$, where e is a unit charge. An ion like the hydroxyl ion, made up of two atoms, must of necessity have a dipolar configuration, besides having its unbalanced charge.



Summarizing, therefore, kaolinitic minerals are 1:1 lattice type minerals having low affinity for water and low surface activity. They have a very low base-exchange capacity, and show very little tendency toward swelling when wetted.

Montmorillonitic clay minerals have 2:1 type lattices inasmuch as their lattice is composed of two hydrated silica sheets with their vertex (OH) groups pointing toward each other and a gibbsite sheet sandwiched between them. The formation of the montmorillonite crystal may be considered as exactly similar to the formation of the kaolinite crystal, but with the condensation process that links a hydrated silica sheet to the gibbsite sheet taking place on both sides of the gibbsite sheet instead of merely on one side. The two hydrated silica sheets are, therefore, joined to the gibbsite sheet by shared oxygen bonds. Such a montmorillonitic crystal whose lattice structure consists of a pure gibbsite layer sandwiched between two pure hydrated silica layers is called an ideal montmorillonite. (See Figure 9, page 120) Only very rarely does a natural montmorillonite show evidence of possessing this ideal structure. By far the more common montmorillonites are the so-called "substituted montmorillonites". Before reverting to a consideration of the structure of substituted montmorillonites, however, it may be mentioned that, as in the case of kaolinite, the ideal montmorillonite structure is electrically neutral except for unsaturations along broken edges. However, even in the case of ideal montmorillonites two factors combine to make this mineral more active than kaolinite. The presence of one more silica layer per crystallite would tend to increase the edge adsorbability in comparison with that of the kaolinite structure, and the presence of two oxygen sheets per crystallite gives an increased chance of hydroxyl ion adsorption. Furthermore, unit crystals of ideal montmorillonite stacked over each other are held together only by very weak secondary forces acting between the opposing oxygens of the silicon-oxygen tetrahedra; it follows, therefore, that this type of clay mineral is more readily dispersed into smaller particles than kaolinite.

Accurate analysis of montmorillonites usually reveals the presence of varying amounts of magnesium and iron, which should not occur according to the ideal structure, and variations in the ratio of aluminum to silicon are frequently found. These discrepancies are explained by the theory that in nature certain substitutions have taken place within the lattice. If ferric atoms, which are trivalent, are substituted for the aluminum atoms of the gibbsite sheet, the lattice structure remains electrically balanced. However, if magnesium atoms, which are divalent, are substituted for the aluminum atoms of the gibbsite sheet the lattice takes on a net negative charge. In this case, the negative charge is located in the gibbsite sheet, that is, in the middle of the particle, and, therefore, the force of attraction for cations effective at the surface of the particle is relatively small. On the other hand, an increase in the ratio of aluminum to silicon over the theoretical ratio can only be explained by the assumption that some of the silicon atoms of the silica sheet have been replaced by aluminum atoms. This substitution also makes the particle acquire a net negative charge in view of the fact that tetravalent silicon has been replaced by trivalent aluminum; but in this case, the negative charge is located in the silica layer which is close to the surface of the particle, and, therefore, the resulting attraction for cations is relatively strong. Figure 13, page 120, shows a substituted montmorillonite in which one of the four aluminum atoms of the gibbsite layer has been replaced by a magnesium atom, resulting in a net unbalance of one negative charge. Substitutions in the layer of silicon atoms are somewhat less common but quite possible: such a substitution is shown in Figure 12 which is actually an illite (mica) -- a montmorillonite which owes most of its charge to substitutions in the silica layer approaches an illite.

Considering the substituted montmorillonites as they exist in nature, it is obvious that the particles possess adsorbed cations in a measure sufficient to balance the net negative charge: the law of least free energy requires it. Cations are primarily adsorbed on the surfaces of the silica sheets, about 80 per cent of the exchange positions of montmorillonite being on these surfaces. Broken oxygen bonds and the possibility of some replacement of hydrogen of hydroxyls at the edges of flakes account for the rest of the exchange capacity. In nature a cation very commonly found associated with montmorillonites by such adsorption, is sodium. A montmorillonite containing loosely adsorbed cations, if placed in pure water builds up a double layer without the need of electrolyte. The actual behavior of the clay will depend on the adsorbed cation, but in general it can be stated that the cations on hydration will dissociate to a certain distance from the surface of the particle and form the counterions of the diffuse double layer. Since most of the cations are adsorbed on the surfaces of the crystallites, they will tend, on hydration, to pry apart the units held together loosely by weak secondary O-O bonds. It has been pointed out before that such hydration of adsorbed cations helps to break up clay particles down to the ultimate particle size when dispersed in water. The effect of dispersing agents is, therefore, not as pronounced with montmorillonite as with kaolinite because the particle size of montmorillonite in a suspension is already at a minimum and the formation of the double layer does not depend on adsorption of ions from the dispersion medium.

The hydration of the adsorbed cations is also said to account for the high degree of swelling of montmorillonitic clays; a sodium montmorillonite has reached, by swelling, a c-dimension* (thickness) thrice the normal dimension. The amount of expansion of the montmorillonite lattice depends on the exchangeable cation carried by the particles. The amount of water between crystallites varies, within limits, depending on the amount of water available for the clay to absorb, and there is a corresponding variation in the c-dimension of the unit cell; the mineral is, therefore, said to have an expanding lattice.

In short, therefore, the montmorillonitic minerals have 2:1 type lattices which exhibit variation in one dimension with change of water content. They are characterized by very high surface activity and exchange power, base-exchange capacity being between 60 and 100 milliequivalents per 100 grams of clay. They have a high affinity for water and swell to a very marked degree.

Illites have a basic structure identical with that of ideal montmorillonite. Whereas montmorillonites usually show substitutions of magnesium for aluminum in the gibbsite sheet, resulting in net negative charges located in the center of the crystallite, illites exhibit a marked degree of substitution of aluminum for silicon in the silica sheets, resulting in negative charges close to the surface of the particle. Some montmorillonites show some such substitution of aluminum for silicon and thereby approach the illites, unless the effect of this substitution is partly balanced by adjustments in the gibbsite sheet. But illites do not show the variable spacing exhibited by the montmorillonitic minerals, and have little tendency to swell. How is this difference between illites and montmorillonites explained?

The fact that the negativity of the particle has its source very near the actual surface of the parcel causes the setting up of fairly strong attraction forces for positive charges. The cations that are adsorbed are held fairly strongly. In nature it is found that potassium ions are usually associated with illites. Considerations of size of exchangeable ions are used to explain this predominance of

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* The c-axis is perpendicular to the sheets in the clay mineral lattice. The height of the ultimate particle of montmorillonite, without water between units, is 9.6 Å. Maximum recorded expansion has given a c-dimension of 30 Å. It might be noted that pyrophillite (ideal montmorillonite) has a c-dimension of 9.2 Å. The increased height of the montmorillonite cell is explained by the presence of cations between the units.

potassium ions in illites. Of the common ions, the potassium ion is the only one which is of a size larger than the hole in the silica sheet, (see page 113) and, therefore, cannot penetrate into the structure. The potassium ions adsorbed on the surfaces of the crystallites act as bridges between adjacent particles, thus preventing a particle stack from being swelled by water entering between the parcels. Such adsorbed potassium ions are rather difficult to replace. In spite of substitutions in the illite lattice, the seat of much of the exchange capacity of illite is at flake edges. Many of the cations held between basal planes because of lattice replacements are not exchangeable, partly because illite does not break down readily into small parcels.

Extreme cases in which the replacement of silicon by aluminum in the silica sheets reaches a maximum and the adsorbed cations are entirely potassium ions, represent the practically inert mica. Illites take up positions intermediate between mica and highly plastic montmorillonites, depending on their structure. The greater the replacement of silicon by aluminum in the silica sheets, the closer the illite will resemble mica in its properties. Replacements of aluminum by magnesium in the gibbsite sheet are also found in illites, and the results of such changes in the ideal illite structure are similar to those occurring in altered montmorillonites. The lower the degree of replacement in the silica sheets and the greater the substitution of magnesium for aluminum in the gibbsite layer, the more closely will the illite resemble montmorillonite in behavior.

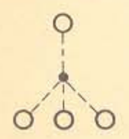
In short, therefore, illites are minerals of the 2:1 type lattice. Their properties are in most respects intermediate between those of kaolinites and those of montmorillonites. Their base-exchange capacity is about 30-50 milliequivalents per 100 grams of clay.

STRUCTURAL DATA OF CLAY MINERALS

The schematic drawings in the first columns represent the composition of the unit cellof the crystal lattice. All atoms are projected into one plane. The second column gives the number and type of atom or group in every lattice plane. The third column reveals the amount of available or needed electrons in every sheet. If the (+) and (-) in this column compensate each other, the crystal is electrically neutral. If they do not, the lattice carries either a positive or negative charge. As the plus andminus charges are listed for every layer, it is easy to determine where the unbalance actually occurs in the lattice.

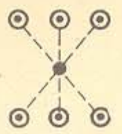
Taken from "Colloid Chemistry in Ceramics" by E. A. Hauser, Journal American Ceramic Society, 24, 179 (1941).

1 - SILICON TETRAHEDRON



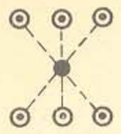
1 O	-2
1 Si	+4
3 O	-6

2 - ALUMINUM OCTAHEDRON



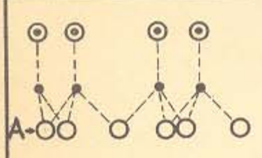
3 OH	-3
1 Al	+3
3 OH	-3

3 - MAGNESIUM OCTAHEDRON



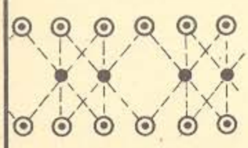
3 OH	-3
1 Mg	+2
3 OH	-3

4 - HYDRATED SILICA



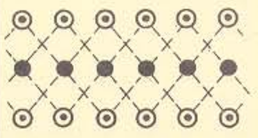
4 OH	-4
4 Si	+16
6 O	-12

5 - GIBBSITE



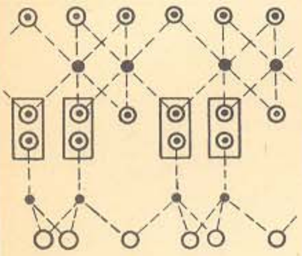
6 OH	-6
4 Al	+12
6 OH	-6

6 - BRUCITE



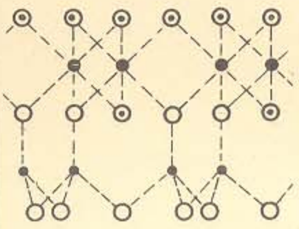
6 OH	-6
6 Mg	+12
6 OH	-6

7 - HALLOYSITE



6 OH	-6
4 Al	+12
6 OH	-6
4 OH	-4
4 Si	+16
6 O	-12

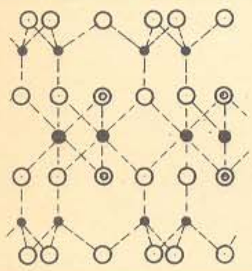
8 - KAOLINITE



6 OH	-6
4 Al	+12
4 O 2 OH	-10
4 Si	+16
6 O	-12

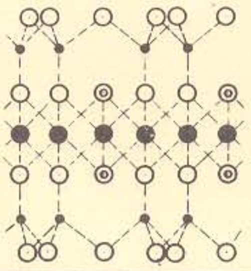
· - Si
• - Al
● - Mg
○ - O
⊙ - OH

9 PYROPHYLLITE AND MONTMORILLONITE (IDEAL CASE)



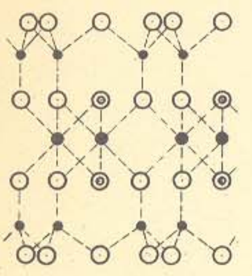
6 O	-12
4 Si	+16
4 O + 2 OH	-10
4 Al	+12
4 O + 2 OH	-10
4 Si	+16
6 O	-12

10 TALC



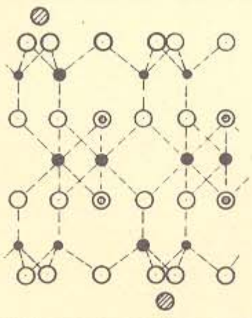
6 O	-12
4 Si	+16
4 O + 2 OH	-10
6 Mg	+12
4 O + 2 OH	-10
4 Si	+16
6 O	-12

11 NONTRONITE



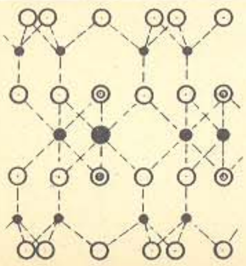
6 O	-12
4 Si	+16
4 O + 2 OH	-10
4 Fe^{+++}	+12
4 O + 2 OH	-10
4 Si	+16
6 O	

12 MICA (ILLITE)



1 K	+1
6 O	-12
3 Si + 1 Al	+15
4 O + 2 OH	-10
4 Al	+12
4 O + 2 OH	-10
3 Si + 1 Al	+15
6 O	-12
1 K	+1

13 MONTMORILLONITE (SUBSTITUTED)



6 O	-12
4 Si	+16
4 O + 2 OH	-10
3 Al + 1 Mg	+11
4 O + 2 OH	-10
4 Si	+16
6 O	-12

· - Si
• - Al, Fe^{+++}
● - Mg
○ - O
⊙ - OH
▨ - K

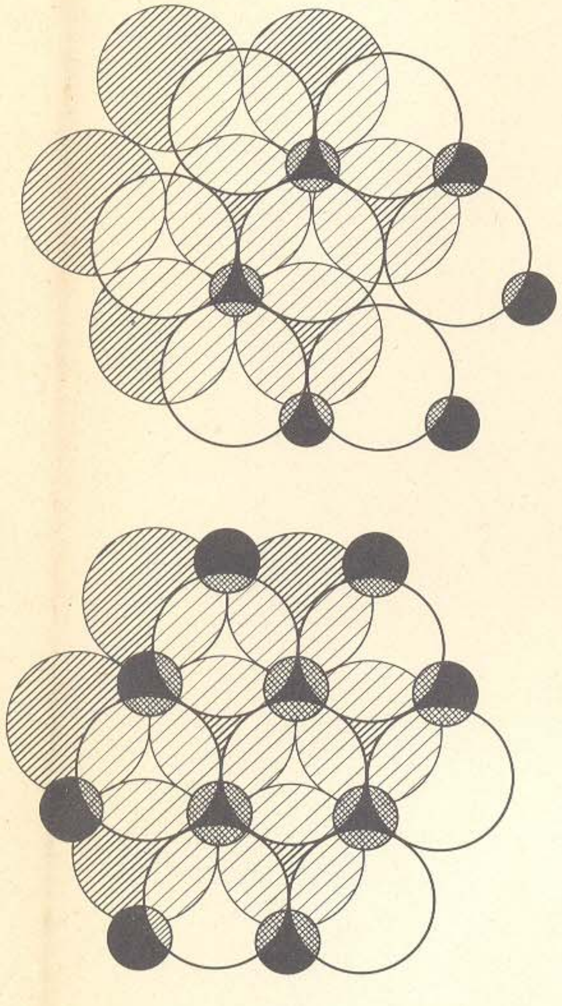


Fig. 14. (Bottom) Brucite $Mg(OH)_2$ (schematic); the hydroxyl groups constituting the upper layer have been drawn transparent so that the location of the magnesium atoms sandwiched between the two hydroxyl layers may be seen clearly. (Top) Gibbsite $Al(OH)_3$ (schematic); the hydroxyl groups in the top layer have been drawn transparent to show the location of the aluminum atoms sandwiched between the two staggered layers (compare positions of Al with those of Mg in bottom figure).

Taken from "Colloid Chemistry in Ceramics" by E. A. Hauser, Journal American Ceramic Society, 24, 179 (1941).

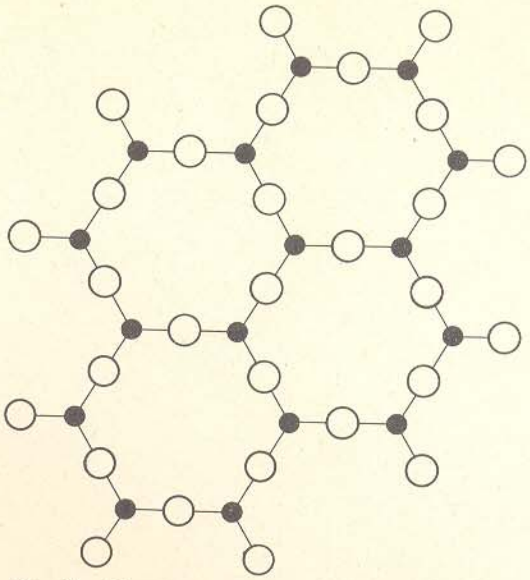


Fig. 15. Structure of a symmetrical silicon-oxygen sheet (schematic); only one plane shown.

Taken from "Colloid Chemistry in Ceramics" by E. A. Hauser, Journal American Ceramic Society, 24, 179 (1941).

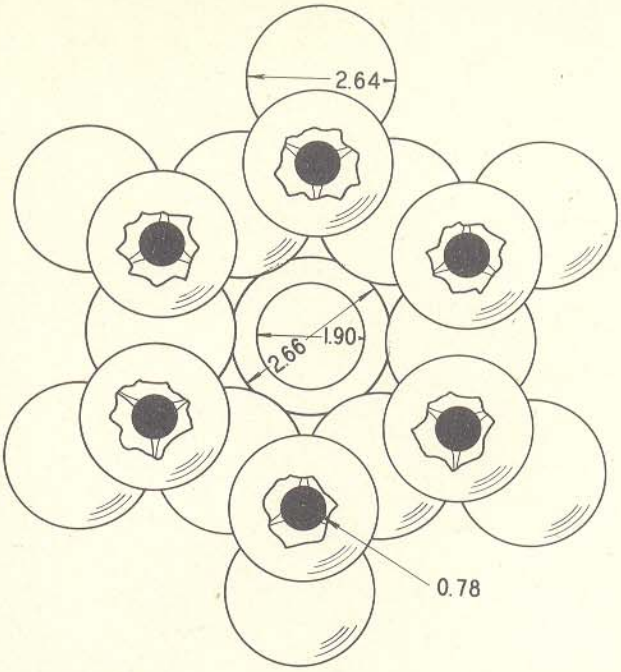


Fig. 16. Hexagonal arrangement of silicon-oxygen tetrahedra in a silica sheet (top view, schematic); the top oxygens have been cut open to show the location of the silicon atoms; into the center space two concentric circles have been drawn. The larger one corresponds in diameter to a potassium atom, the smaller one to a sodium atom; the actual dimensions in Angstrom units for the different atoms are indicated.

Taken from "Colloid Chemistry in Ceramics" by E. A. Hauser, Journal American Ceramic Society, 24, 179 (1941).

ABSTRACTED ARTICLES, PATENTS, AND THESES

This chapter is an attempt to cover some of the many articles which have not been mentioned elsewhere in this report and which are nevertheless of the greatest importance in furnishing a necessary background for research on chemical soil solidification. Complete coverage can in no way be guaranteed. It must further be accepted that the selection of these few important articles as representative of the great number that were read, and even greater number that are available, is based on a personal opinion, and, therefore, is very much subject to criticism. It is felt, however, that this chapter is of considerable value in this report, in spite of its limitations. The abstracts were prepared mostly with the aim of presenting whatever seemed to be new and/or important ideas in the original articles. In many cases the abstracts, therefore, resolve themselves into transcriptions of important statements from the originals.

Endell, K. and Hoffmann, U., "The Chemical Nature of Clays," International Conference on Soil Mechanics, Vol. 1, p. 51, 1936.

In montmorillonite swelling is also due to expansion of lattice: however, the intracrystalline change in the space-lattice plays only a minor part in the visible swelling of clays which is caused chiefly by the fixation of water by the cations attached to the surfaces of the clay particles. The fact which has been observed and investigated by A. Casagrande that many soils have a smaller bearing capacity in a disturbed than in an undisturbed state is probably to be explained at least in part by the thixotropic properties of the clays.

Hauser, E. A. and Le Beau, D. S., "Studies on Gelation and Film Formation of Colloidal Clays," Journal Physical Chemistry, Vol. 42, p. 961.

Although it cannot be denied that gelation is facilitated in many cases where the disperse phase consists of organic molecules joined, by primary valences, in chains of high molecular weight, or where condensation leads to chain-like aggregates, we have ample evidence that such a structure is not essential for an explanation of all types of gelation.

Contrary to previous assumptions, the detection of any ultramicroscopically visible specific alignment or grouping of the disperse phase was not possible. On addition of electrolyte, one observes a decrease in displacement due to Brownian motion, without any alignment, grouping or any specific structure. Upon reaching a certain concentration of electrolyte Brownian motion ceases entirely. If only a slight excess of electrolyte is added, one observes the formation of "ultra-flocks" separated by narrow channels: this gel-like system persists as long as the flocks are sufficiently loose in structure.

Sols show orientation in polarized light only when in motion, but neither a sol at rest nor a gel is doubly refractive. On the basis of such a concept gelation must become more pronounced, the smaller the particles, because a system of a given volume can be considered the more volume-dispersed the more particles are available. Maximum gelation will exist if the particles are of uniform size and uniformly spaced (a system of random orientation but great regularity of distribution).

If a gel is spread on an appropriate support and allowed to dry out, we observe that the particles when forced closer together line up or actually snap into their new location, forming long, interlacing filaments or fiber bundles. The presence of separate reflection disks as observed in the sol and gel stage, gives way to continuous thread-like aggregations, which upon continued evaporation seemingly grow into larger crystals of highly anisometric shape. These filaments interweave and tie together by tridimensional cross-linkages resulting in a coherent network or structure. After complete desiccation an absolutely self-supporting film is obtained, which can be easily removed from its support as a coherent sheet.

Depending on the particle size fractions used, films of varying degree of brittleness and flexibility are obtainable, the latter increasing with decreasing particle size.

Films prepared from sodium-bentonite swell and finally go into solution, if placed in water, whereas films of hydrogen bentonite resist very markedly and only show limited swelling.

If sodium-bentonite films are heated to white heat, they become water-resistant and decidedly stronger, the flexibility decreases, and they closely resemble mica in appearance and properties. If the films are subjected to high pressure they become transparent and much stronger.

Hauser, E. A., "Inorganic Film Products and Method of Making Same," United States Patent #2,266,636, December 16, 1941.

The ability of inorganic materials to form self-supporting coherent flexible films apparently depends upon their ability to form gels due to the presence of strongly hydrated highly colloidal matter.

Hauser, E. A., "Waterproofing and Flexibilizing Clay Films," United States Patent #2,266,637, December 16, 1941.

It will be understood that whether the sol or the gel is used as the film forming material, the gel stage immediately precedes the solid state.

Lead acetate treatment produces the double effect of rendering the films water resistant and stronger. Treating time varies inversely with the temperature of the treating agent.

Agents for flexibilizing:- Consideration of the character and effects of the treating agents which are operable compared to other chemicals which are not operable indicates that the molecules or the active ions of the treating agents must, in both cases, be of such a character as to be able to enter the lattice structure of the material or to neutralize the electric surface charge of the clay particles. In the case of the agents serving to render the films water resistant, the action of the agent, if it is present in the form of a true solution, appears to consist of a base-exchange reaction between the exchangeable cation of the silicate and the cation of the treating agent. If it is a colloidal dispersion, the action appears to be caused by electric neutralization of surface charges. In the case of the agents which serve to render the films more flexible, the theory may be advanced that the molecules of the treating agent enter the lattice structure of the silicate and serve to lubricate it. It appears that the operability of the agents for rendering the films water resistant depends upon their ability to change the electrokinetic characteristics of the silicate. It appears, from a comparions of the diameters of the cations of effective agents with the cations which are capable of base-exchange with the exchangeable base of the hydrous oxide but are not effective, that the cations which are effective have a fairly definite minimum diameter whereas the non-effective cations have a substantially smaller diameter. In the case of montmorillonite, the minimum diameter of the cations of effective agents appears to be about 2.6 Å, or at least about as large as the spacing between the opposite oxygen atoms in the hexagonal silicon-sheet of the unit crystal. Such cations apparently enter the films by base-exchange and are bound by residual valencies and serve to bind adjacent unit sheet-parcels together whereas smaller cations, even though they may enter the film by base-exchange and become fixed in the lattice structure by residual valencies fall into the internal structure of the lattice and remain free moving in the space available and do not bind the adjacent unit sheet-parcels together.

Both inorganic and organic agents are effective in providing water-resistance. Acids were not found to be very effective: anions are of secondary importance, and the prime requisites of the operable compounds are that their cations shall be capable of base-exchange with the exchangeable base of the silicate and that the compound shall be sufficiently soluble in water.

A generalization is made that those organic compounds which are at least partially soluble in water and do not contain an aromatic ring or a side chain in the middle of the molecule are effective in improving flexibility. The molecule of the treating agent apparently must be free of any group which results in steric hindrance and prevents the molecule from entering the aluminum silicate lattice.

Hauser, E. A., "Method of Waterproofing Inorganic Hydrous Oxide Bodies, and Product," United States Patent #2,317,685, April 27, 1943.

The properties of bentonite films particularly the waterproofness, humidity resistance, etc., may be improved by treatment with the salts, which, upon heating, are capable of forming basic salts, of cations having a diameter greater than 2.64 Å with anions of organic acids containing up to about six carbon atoms per molecule. Suitable cations are those of lead, potassium, barium, strontium, rubidium, caesium, thallium, gold, and ammonium, and suitable anions are those of the fatty acids containing up to six carbon atoms, e.g., formic, acetic, propionic, butyric, caproic, and valeric.

The non-swelling property is attributed to base-exchange of the cation of the treating salt. At the same time the films are rendered resistant to the absorption of moisture from the atmosphere, and these latter effects are attributed principally to the anion of the treating salt. These properties tend to improve as the number of carbon atoms in the anion of the treating salt increase up to four, and this improvement is attributed to the increasing hydrophobic properties of the anions as the number of carbon atoms increase. The humidity resistance of the treated films appears to be proportional to the water insolubility of the salt used as treating agent. The effects produced with anions having different numbers of carbon atoms, i.e., different lengths of the carbon chain, indicate that the anion penetrates the film structure and acts as a bond, thereby strengthening it. Decreased strength and increased brittleness of the hydrous oxide body, found when the anion of the treating agent possesses five or more carbon atoms, is presumably due to the size of the anion, which results in setting up strains in the lattice structure.

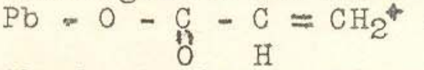
Hauser, E. A., "Method of Waterproofing Hydrous Oxide Bodies, and Product," United States Patent #2,383,647, August 28, 1945.

Lead acrylate and other cation-acrylates where cations are larger than 2.64 Å diameter are suggested for use in waterproofing the bentonite films. The cation of the treating salt, by base-exchange, replaces the hydratable cation of the hydrous oxide (e.g. sodium) by a non-hydratable cation which, due to its size relative to the size of the openings in the silicon-oxygen sheet, serves to bond the hydrous oxide unit parcels together and thereby prevent swelling of the hydrous oxide body when contacted with water. The cation of the treating salt does not, however, prevent water from entering the hydrous oxide structure, i.e., it does not prevent moisture pick-up. The polymerizable organic anion of the treating salt which is bonded to the cation yields, when polymerized, a highly hydrophobic water-insoluble material which seals the hydrous oxide film structure against the entrance of water and thus gives the film its low moisture pick-up characteristics. The high temperature of the solutions of the treating salts employed favors high concentration of the solution and thus favors impregnation and incorporation of relatively large amounts of the treating salt into the hydrous oxide structure.

It will be understood, of course, that the anion of the treating salt should be capable of polymerization to yield a highly hydrophobic product so as to exclude moisture from the hydrous oxide structure. This property is characteristic of polymerization products of the polymerizable organic acid anions.

Hauser, E. A., "Molding Composition, Molded Product, and Method of Making," United States Patent #2,401,348, June 4, 1946.

The sodium-bentonite may be treated with a solution of lead acrylate so as to substitute a complex lead-acrylate cation for the sodium ion of the bentonite by base-exchange and the resulting bentonite-lead acrylate molecule polymerized to yield a product having excellent properties. It appears that in addition to the lead acrylate ion which is introduced into and chemically combined with the bentonite by base-exchange, additional lead acrylate may be simply adsorbed and/or absorbed on the bentonite particles, and that in the polymerization this additional lead acrylate becomes chemically combined by polymerization of its acrylic group with those bonded to the bentonite.

It appears probable that in concentrated solutions we may consider the base-exchange as having occurred between the exchangeable sodium of the bentonite and the complex  $Pb - O - \underset{\overset{\|}{O}}{C} - \underset{H}{C} = CH_2^+$ ions. The net result is two-fold; first the bentonite particles are rendered non-swelling in water due to the replacement, on the surface planes, of the sodium ions which have a small ionic radius by ions having a much larger ionic radius, and second, the edges and corners of the bentonite particles are coated by base-exchanged lead acrylate ions. The lead acrylate ions besides being held to the surfaces also get in between the unit crystal sheets constituting a bentonite particle so that upon polymerization of these acrylate groups the originally open-textured bentonite becomes filled and firmly bonded together by true chemical bonds.

Whittaker, H., "Effect of Particle Size on Plasticity of Kaolinite," Journal of the American Ceramic Society, <u>22</u>, 16 (1939).

Plasticity is directly related to surface area and inversely related to particle size. Kaolinite under the conditions of test as outlined exhibits plasticity only when the surface area is greater than 180 x 10^4 sq. cms. per 100 grams of clay. The thickness of water films at optimum plasticity is of the order of magnitude of 90 Å. When hydrogen is exchanged for the bases, the plasticity increases. The removal of the exchangeable bases increases the water required to form a plastic mix of kaolinite. The plasticity of kaolinite is not due to a coating of colloids on the surface of the particles but is exhibited only when the particles contained in the system, or a sufficient amount of the particles, are of colloidal dimensions. The drying shrinkage increases, in general, with decreasing particle size until a maximum is reached: then dry strength decreases. When hydrogen is exchanged for the bases the dry strength decreases.

Grim, R. E., "The Clay Minerals in Soils and Their Significance," Proc., of the Purdue Conference, p. 216, September, 1940.

Endell has found that the relative abundance of exchangeable bases is important. For example, as the amount of sodium approaches the total exchange capacity, the bonding power of a montmorillonite clay first increases and finally decreases.

Jewett, T. M., "Sorption by Clays," Soil Science, 50, 163 (1940).

Adsorption of water in unimolecular layers does not appear to be of first importance in sorption. Mattson calculated that hygroscopic moisture was sufficient to provide a layer 16 mols. thick (estimating total available surface). Clays will, in general, sorb water in a dual manner. 1) As they are porous solids of large surface area, they will sorb water vapor by condensation processes (any condensable vapor). 2) They can also take up water vapor by forces which are specific to water, for example, as water of lattice swelling in the particular case of montmorillonite, as water associated with exchangeable bases, or as water of hydration of admixed sesquioxides.

The differences, water sorption minus toluene sorption, are shown to be related to the silica-sesquioxide ratios of the clays.

At a higher level of moisture content sodium-clay was found to hold much more "imbibitional" water than calcium-clay, a difference which is not appreciable at lower moisture contents among common cations--excepting potassium which has a marked effect on hygroscopicity over thirty per cent H_2SO_4 (i.e., at low moisture contents).

The importance of the fundamental differences between the behavior toward water of montmorillonite and kaolinite clay types is stressed. The sorption of toluene is regarded as a particular instance of the sorption which takes place with any condensable vapor, and which is a measure of such quantities as surface area and capillary distribution. It has been found that soil colloids with low silica contents sorb similar amounts of water and toluene; those with high silica-sesquioxide ratios sorb much more water than toluene.

Puri, Amar Nath; Asghar, A. G.; and Dua, A. N.; "Physical Characteristics of Soils: VI. Influence of Clay Exchangeable Bases and Hygroscopic Moisture on Soil Cohesion," Soil Science, 49, 239 (1940).

Influence of Clay:- The magnitude of the force of cohesion must depend on the points of contact between the particles. Cohesion for the same per cent of clay rapidly falls as the particle size (of the treated material) increases.

Effect of Hygroscopic Moisture and Exchangeable Bases:- The enormous change of cohesion due to the drying of the hygroscopic moisture leads one to the conclusion that beyond a certain degree of wetness the cohesive forces in soils are partly molecular and, therefore, might be associated with the nature of the exchangeable ion in the clay complex.

The effect of exchangeable bases on soil cohesion is maximum when the soil is dry. The absorption of moisture leads to a narrowing of the differences due to ions. The order of cohesion for the dry soils follows the generally accepted order of dissociation for these ions. (sodium, potassium, magnesium, calcium, hydrogen) The relation between moisture content and cohesion is substantially the same, whether the soil is gradually dried or rewetted.

The greater cohesion in sodium and lithium soils (in comparison with other single base-soils) may be due to a stronger bond between the dissociated ions, or it may be caused by the enhanced dispersion of the clay particles. The latter is more probable. The high dispersion would result in a larger number of points of contact. If soil is first completely dispersed and then converted into an hydrogen soil by acid treatment and different ions are introduced as hydroxides without allowing the soil to dry, the cohesion is enormously increased over that of the undispersed soil. Although the amount of conventional clay in a dispersed soil was the same whatever the nature of the cation introduced, this was not true of particles finer than clay, which showed a higher percentage in the case of sodium and lithium soils: these finer particles would easily account for the greater cohesion in sodium and lithium soils.

Effect of Flocculation with Calcium Chloride on Cohesion of Sodium-soil:- The results show that the presence of calcium chloride causes substantial reduction in the cohesion of the dry soil. The effect of calcium silicate in higher per cent treatments is remarkable--probably because of formation of calcium silicate crystals which are responsible for the increase of cohesion.

Effect of Driving Away Water of Constitution by Heating to Different Temperatures:- The cohesion first drops off (to about 400°C.) and then increases, at 800°C. having about the same cohesion as when dried by H_2SO_4.

Effect of Glycerine and Sugar:- These are supposed to increase ionization of acids, therefore, cohesion of hydrogen soil should increase in the presence of these. At $pH \approx 7.5$ the maximum effect was noted: the strengthening action was remarkable.

Effect of Molasses:- (tried on sodium and calcium soil) Dry cohesion is increased. The maximum effect is obtained with about two per cent molasses. Cohesion decreases on rewetting.

Endell, Kurd, "The Swelling Capacity of Clays in the Construction Foundation and Its Technical Significance," (translated from) Die Bautechnik, 19,19 (May 2, 1941).

Swelling Capacity was directly determined in the enslin apparatus. Kaolin among the clay minerals has the smallest water absorption power, but the greatest capillary speed. The most severe frost heaving is shown by quartz dust, then comes kaolin, and the least is shown by bentonite. For the frost heaving of clay soils, there are two ranges: 1) the range of the kaolinite-containing soils, more or less uninfluenced by permeability 2) the range of the bentonite-containing soils, controlled by permeability.

Johnson, A. L., and Lawrence, W. G., "Fundamental Study of Clay: IV Surface Area and Its Effect on the Exchange Capacity of Kaolinite," Journal of the American Ceramic Society, 25, 344 (1942).

A linear relationship is shown to exist between the surface area and the base-exchange capacity for all of the sizes studied.

Ensminger and Gieseking, "The Absorption of Proteins by Montmorillonitic Clays and Its Effect on Base Exchange Capacity," Soil Science, 51-52, 125.

The absorption of proteins by montmorillonitic clay is a good means of studying further effects of organic material on the base-exchange capacity of clays. Gelatin and barium were used in studying the base-exchange capacity of complexes.

The amount and nature of the protein added determine the magnitude of the reduction in base-exchange capacity. There is no reduction in an alkaline medium as the pH value is lowered, the base-exchange capacity decreases. The fact that a decrease in hydrogen ion concentration increases the basic properties of proteins would indicate that they are absorbed as cations.

Treatments altering basic properties of proteins cause them to be less absorbed.

An increase in hydrogen ion concentration resulted in greater absorption due to greater ionization of the amino groups. These data would indicate that proteins are partly absorbed as cations.

Sideri, D. I., "On the Formation of Structure in Soil: II Synthesis of Aggregates; on the Bonds Uniting Clay with Sand and Clay with Humus," Soil Science, 42, 461.

Adsorption of Clay by Quartz:- Observations point to the possibility of the clay's condensation on the quartz in the shape of very tenacious pellicles which are not dissolved in water. Adsorption of clay on quartz may take place on the basis of the similarity of the crystalline periods of quartz and clay. Such adsorption was found to be an irreversible state furthering cohesion: this process is due to the fact that orientation is not limited to one or two layers of molecules, but extends much farther, one layer of molecules tending to orient the next, until orientation is fixed and there is no disorientation.

The Bond Between Clay and Quartz Sand:- The ability of sand to assume the form of grouping belonging to clay is explained by the similarity of their forms of orientation. The smectic phase of clay possesses a partially periodical structure, the periods of which coincide with the crystalline periods of quartz. The tenacity of the "intergrowth" does not depend, therefore, on the nature of the absorbed cations and of the lyospheres determined by them.

A remarkable result of these experiments on synthesizing aggregates is that we were able to obtain a tenacious watertight structure from highly hydrated sodium-clays.

Adsorption of Humate on Quartz Sand:- Considerable.

Bond Between Humus and Clay:- A certain amount of organic substance is most firmly bound with clay. A remarkable property acquired by clay under the influence of humus is the decrease of its solubility. Clay without previous drying is able to bind humate irreversibly in considerable amounts greatly exceeding the quantity necessary for the formation of the adsorption layer. This suggests mutual orientation, similar to that of the sand-clay system. Solubility of clay is decreased under the influence of insignificant amounts of humus, and drying increases the irreversibility of humate. A possible explanation of this is the formation of an adhesion layer and the orientation of the molecules at the surface of quartz sand mixed with clay.

The former conception that the particles forming the soil structural aggregate are held together by the tension of the water film is supplemented by the finding that the surface film creates a definite orientation of the particles in relation to one another. The explanation of the tenacity of the bond lies in the stability of the group arrangement of the particles: the most stable arrangement of particles is the homogeneous one.

Siefert, A. C. and Henry, E. C., "Effect of Exchangeable Cations on Hydrophilic Nature of Kaolin and Bentonite," Journal of the American Ceramic Society, 30, 2, February, 1947.

Affinity for water of a kaolin and bentonite saturated with hydrogen, calcium, sodium, potassium was studied by (1) heat of wetting as determined by calorimetric measurements (2) sorption of water from the vapor phase by weighing (3) desorption or removal of water by differential-thermal analysis. It was shown that hydrogen and calcium clays had a greater affinity for water than sodium and potassium clays. Although the bentonite evolved more heat and sorbed more water per gram of clay, it evolved less heat and sorbed less water per milliequivalent of exchangeable cation than did the kaolin; the differences in the effects of various cations were more pronounced in bentonite than in kaolin. The results may be explained as follows from considerations of the mineral structures: (1) a greater amount of water hydrates the surface of kaolinite in proportion to that hydrating the exchangeable cations than is the case in montmorillonite, and (2) the exchangeable cations may be hydrated to a greater degree (i.e., less strongly held) on kaolinite than on montmorillonite.

The plastic properties of clay may be explained in part by the concept of a film of water around the clay particles. Most clay minerals, in general, are composed of flake or fibrous-shaped particles; these particles in the clay-water system are enclosed by water hulls and these hulls determine to a great extent the plastic properties of the system. The form which the water assumes is influenced by a combination of factors, including (a) the structure of the clay mineral (b) the shape and surface area of the particles (c) the type, concentration, and hydration of the adsorbed ions, and (d) the presence of organic matter.

State of Water Hull:- The state of water hull has often been viewed as built up of layers of oriented dipolar molecules. However, if heat of wetting appears only as a consequence of the compression of the water on the surface of the particles values must be negative if the measurement is carried out below 4°C. This has not been obtained.

The degree of hydration of ions in free solution must not be confused with the hydration of adsorbed ions. Jenny states that the effective value of the radius of adsorbed ions is probably somewhere between the crystal-lattice radius and the hydrodynamic radius. Also possibly the polarizing effect of adsorbed cations on the water would affect the outer hull. The polarizing effect is stronger, the greater the charge and the smaller the radius of the ion.

The adsorbed cations may affect the water film in several ways other than by their hydration. When a large ion is adsorbed there would remain a smaller space for water molecules than if a small ion were adsorbed. Since two monovalent cations are required to replace one divalent, it seems that clays base-saturated with divalent cations would be more highly hydrated than those with monovalent cations of similar size. As the hydrogen ion is the smallest of all, hydrogen clays would be most highly hydrated.

Also the ideas of Pauling relating to isomorphous replacement are discussed. According to them, for example, the replacement of $2Na^{+} + 2H_2O$ by $Ca^{++} + 3H_2O$ would be permitted.

If the hydrophilic nature of clays were to be attributed solely to the hydration of the exchangeable cations, it would have to be concluded that these ions are hydrated to a greater degree in kaolin than in bentonite: i.e., such cations would appear to be less strongly held by kaolin. On the other hand, if the degree of hydration of the adsorbed ions were the same in both, the additional hydration of kaolinite per me. of exchangeable cation must be attributed to some other cause, e.g., that a greater amount of water hydrates the surface of kaolinite in proportion to that hydrating the cations, than is the case in montmorillonite, i.e., a greater fraction of the surface of montmorillonite would contain active areas on which cations would be adsorbed, with the result that proportionately less surface would remain exposed to water alone. Either or both assumptions might be valid.

The hydrophilic nature of clays seems to play an important role in controlling the properties of clay-water systems when only a small amount of water is present, i.e., when clay-water ratio is high. The effect of the interaction of repulsive and attractive forces between particles may become more important when an excess of water is present.

Winterkorn, H. F., and Baver, L. D., "Sorption of Liquids by Soil Colloids: I, Liquid Intake and Swelling by Soil Colloidal Materials," Soil Science, 38, 4, 291 (1934).

Although the exact nature of water sorption is not completely understood, the original assumption was made in this study that part of the water is taken up to fill the macro and micro-pores and that the remaining sorbed amounts are used to produce swelling. Since certain non-polar liquids such as benzene do not cause significant swelling when sorbed by soil colloids, they can be used to measure the pore space of the system. On the basis of these assumptions the amount of swelling water would be approximately the difference between the sorbed amounts of water and benzene.

The amount of sorption should be expected to vary with the nature of the sorbing surface and the properties of the sorbed liquid. Experiments were designed to employ (a) colloids of varied chemical constitution both as to their crystal lattice compositions and as to the nature of the ions adsorbed upon the colloidal surfaces (b) liquids possessing a wide range in their dielectric properties but maintaining a certain similarity in their molecular structures.

Effect of dielectric constant and molecular structure on the sorption of liquids, investigated both for non-polar liquids and for water and various alcohols, showed that a relationship between swelling and dielectric constant of liquid exists only if there is certain similarity in molecular structure of liquids.

Russell, E. W., "The Interaction of Clay with Water and Organic Liquids as Measured by Specific-Volume Changes and Its Relation to the Phenomena of Crumb Formation in Soils," Phil. Trans. Royal Society, London, (A) 233, 361 (1934).

No evidence could be obtained of interaction between clay and non-polar liquids. Interaction took place in all the polar liquids examined.

Crumb formation is limited to those particles possessing considerable base-exchange capacity. It is not shown by any of the kaolinitic clays of low base-exchange capacity so far examined. Crumb formation is further limited to particles below a certain size. And it is induced only by those liquids the molecules of which have an appreciable dipole moment. The hardness of the crumbs is dependent on the size of the clay particles, of the exchangeable cations and of the molecules of the wetting liquid; only when they are all small, are the aggregates hard. The stability of crumbs depends on the liquid and on the exchangeable cations of the particles: sodium clay aggregates are unstable in water, though stable in dry amyl alcohol; calcium clay aggregates are stable in water, though unstable in dry amyl alcohol.

A clay particle in a dilute suspension can be pictured as consisting of a central core surrounded by a surface carrying a negative charge. Around each negative charge is an envelope of water molecules which are more strongly orientated the nearer they lie to the charge. Outside this surface are the cations, also possessing envelopes of orientated water molecules. Some cations are so close to a negative charge on the surface of the clay particle that the two water envelopes belonging to these charges overlap and the water molecules in this region are very strongly orientated in their joint field. The system may be represented as consisting of links of the nature "particle - dipole - cation - dipole - particle".

Effect of Electrolytes:- (1) Crumbs are smaller and weaker (2) provided the concentration of electrolyte exceeds a certain value all crumbs are stable in the solution of the electrolyte. Both these observations may be attributed to the reduction in dissociation of the cations from the clay surface covered by the electrolyte. Floc formation occurs only when the electrokinetic potential of the clay particle is low (low dissociation of cations): crumb formation occurs when there is an appreciable amount of dissociation of cations from the surface. (High zeta potential) Adding sodium chloride to sodium-clay: the sodium and chloride icns from the added salt also have envelopes of orientated water molecules, therefore, links of the type $(\overset{+}{\text{d}}\text{ipol}\overset{-}{\text{e}})(\overset{+}{\text{sodium}})(\overset{-}{\text{d}}\text{ipol}\overset{+}{\text{e}})(\overset{-}{\text{chloride}})(\overset{+}{\text{d}}\text{ipol}\overset{-}{\text{e}})(\overset{+}{\text{sodium}})(\overset{-}{\text{d}}\text{ipol}\overset{+}{\text{e}})$ occur. This link is longer, can hold much more water and, therefore, becomes effective at much higher water concentrations. The length is responsible for the thixotropic behavior of these rigid suspensions.

Winterkorn, H. F. and Baver, L. D., "Sorption of Liquids by Soil Colloids: II. Surface Behavior in the Hydration of Clays," Soil Science, 40, 5, 403, (November, 1935).

There are important influences contributing to the swelling of clays other than the effect of the exchangeable ions. It seems that the forces within the inner layer can attract to the colloidal surface water molecules as well as ions. Any explanation of the effect of different ions on hydration must take into consideration not only the orienting tendency of the ions for water molecules, the number and kind of ions present and their activities, but also the attractive power of the inner layer for water as it may be affected by ionic adsorption.

Winterkorn, H. F., "Adsorption Phenomena in Relation to Soil Stabilization," Highway Research Board, 343, (1935).

The adsorption phenomena on soil materials are mainly electrostatic in nature.

Affinity for water may be measured as: (1) Amount of moisture adsorbed by the soil from an atmosphere with a well defined partial pressure of water (hygroscopicity) (2) amount of water taken in when the soil is in contact with a free water surface (swelling) (3) viscosity data of soil suspensions (4) heat of wetting of dry soil materials.

Potassium clays show the least affinity for water. Sodium-clay takes in much more water than, say, calcium or hydrogen clays, but the energy involved is smaller: besides, the swelling takes place much more slowly.

Bi- and poly-valent can link the soil colloids together, especially in the presence of organic material.

Menchikovsky, F., "Effect of the Nature of Exchangeable Bases on Soil Porosity and Soil-Water Properties in Mineral Soil," Soil Science, 62, 169 (1946).

The study of the soil-water properties of mineral soils in relation to the sodium/calcium ratio of replaceable cations reveals a close connection between those properties and the sodium/calcium ratio. In soils with a low content of replaceable monovalent cations, the increase in sodium/calcium ratio induces a gradual increase of the capillary rise as well as of the downward water flow.

In soils with a high content of replaceable monovalent cations, the increase in sodium/calcium ratio induces a gradual lowering of the capillary rise as well as of the downward water flow.

Internal surface (Mitscherlich method) increases continuously in accordance with the sodium/calcium ratio of replaceable cations. Non-capillary porosity gradually decreases with the increasing sodium/calcium ratio of replaceable cations and disappears at a certain point.

It is suggested that: (1) these soil-water properties are produced by the change in number and diameter of the "equivalent capillary tubes"; (2) these variations of diameter are due to different degrees of swelling of the soil colloidal clay.

Baver, L. D. and Horner, G. M., "Water Content of Soil Colloids as Related to Their Chemical Composition," Soil Science, 35, 329.

Hygroscopity over 3.3 per cent H_2SO_4 was not appreciably affected by the nature of the colloid but appeared to be some function of the specific surface. Hygroscopicity over 30 per cent H_2SO_4 was affected by chemical composition of the colloid and nature of exchangeable base, increasing with SiO_2-R_2O_3 ratio and with $H > Ca > Li \geqq Mg > Na \geqq Ba > K$.

The total water loss, between saturation over 30 per cent H_2SO_4 and ignition, by clays containing different exchangeable cations followed the order: $H > Mg \geqq Ca > Li > Ba \geqq Na > K$.

Hygroscopicity of the different colloids increased with the SiO_2-R_2O_3 ratio. The combined water decreased with an increasing ratio.

Hofmann, Ulrich, "Recent Advances in the Chemistry of Clay," Die Chemie (Angew. Chemie, Neue Folge) 55, 37-38 (1942).

The water absorption (and especially its maximum value) is dependent on the nature of the exchangeable cations. In very readily swelling bentonites the crystals are in fact subdivided into individual silicate layers. Swelling is not a continuous process, but proceeds only by stages by way of stoichiometric hydrates, in which 1,2,3,4 or 5 monomolecular water layers of about 3 Å thickness are interlaid between silicate layers. The distribution of the water layers within the individual crystal is generally irregular.

When montmorillonite is heated, the power of intracrystalline swelling is lost: it temporarily becomes a micaceous product. The base-exchange power declines on heating even before the swelling power has disappeared; probably because the exchangeable cations in part go into a new combination which permits no further exchange.

Bentonite exhibits an enormous suspension volume, e.g., 50 cm^3 per gram of bentonite. The explanation suggested as most plausible is that the individual component particles are platelets or even individual silicate layers. These form a voluminous jagged frame work resembling a "house of cards", since the thin and extremely light bentonite platelets have too slight a speed of sedimentation to straighten out in opposition to the Brownian movement. Suspension volume and intracrystalline swelling are both dependent on the nature of the exchangeable cations and are affected or influenced in fact by their dissociation power and their hydration. The lower suspension volume of kaolinite is explained by the fact that the crystals of this mineral cannot be subdivided by the suspension medium and always have a much greater thickness in relation to diameter than bentonite particles.

Rapp, Paul and Mizroch, Jacob, "Effect of the Chemical Properties of Soil Fines on the Performance of Soil-Aggregate Mixtures," Public Roads, 21, 193 (1940).

The $SiO_2:R_2O_3$ ratio of soil colloids is controlled by the kind and amount of clay minerals present. Soils with colloids having ratios higher than two, indicating the presence of montmorillonite group clay minerals, tend to have greater volume changes than soils with ratios less than two.

Base-exchange measurements indicate the activity of the binder portion of the soil. The base-exchange capacity of the binder soil was directly related to the service behavior of eighteen road surfaces examined. Surface courses having base-exchange capacity above 2.2 me. per 100 grams of sample were soft and rutted. In general, those having base-exchange capacity below 1.2 me. were corduroyed and did not consolidate. For values of 1.2 me. to 2.1 me. inclusive, the surfaces of the roads were in satisfactory condition.

Winterkorn, H. F. and Eckert, G. W., "Consistency and Physico-Chemical Data of a Loess Pampaneo Soil: II. Properties of Natural and Homoionic Samples of Soils and Clays," Soil Science, 49, 479 (1940).

The liquid limit is a function of both the water affinity of the internal soil surface and the elasticity of the soil skeleton.

Cohesion increases with increase in plastic index. Plastic index is reduced by hydrogen and tri-valent ions. The subsoil showed a remarkable reduction of plastic index with potassium. Note that the topsoil despite its small silica-sesquioxide ratio possesses a high base-exchange capacity probably because of organic matter. A low base-exchange capacity is usually connected with a low cohesion, under comparable conditions of particle size and water content; a high heat of wetting indicates a great affinity for water: these two conditions together indicate very troublesome material. The heat of wetting is only slightly sensitive to the exchange ions present: the effect of ionic substitution on the physical properties of the soil is not likely, therefore, to be very marked. However, greater effects can be expected by the presence in the soil of ions in excess of its exchange capacity.

Winterkorn, H. F. and Eckert, G. W., "Consistency and Physico-Chemical Data of a Loess Pampaneo Soil: I. Physico-Chemical Properties of Samples from Different Depths of a Profile," Soil Science, 49, 73 (1940).

The more surface there is in a soil system, the more lubricant is required; therefore, the higher the clay and colloid content, the higher should, in general, be the plastic limit: on the other hand, the increase of the number of sliding planes with higher per cent fines, should tend to lower to plastic limit values. Also, sorption of clay particles on larger grains (exempting one side of the clay from the need of lubrication) tends to destroy the straight line relation between colloid content and plastic limit.

A large clay content and a large plastic index indicate rather the potential water-holding capacity than the behavior of the natural soil toward the action of water in situ.

The actual behavior of a relatively dry soil toward water can be represented as a dynamic equilibrium between the wetting energy of the water and the cohesive forces at play in the soil system.

The amount and type of organic material exerts considerable influence on the behavior of a soil toward water.

Winterkorn, H. F. and Moorman, R. B. B., "A Study of Changes in Physical Properties of Putnam Soil Induced by Ionic Substitution," Highway Research Board, 21, 415 (1941).

1) Mineral surfaces adsorb liquid films in accordance with the strength and character of the dipole of the component molecules. 2) Swelling of a soil system depends on the number and type of exchangeable cations per unit surface and on the geometrical character of this surface. Plane surfaces hold thicker films with less energy than curved surfaces.

An indicator of the amount of internal soil surface in a system which is a function of the particle size and of the activity of this surface is the Liquid Limit. By definition, the Liquid Limit is that amount of water expressed in per cent per dry weight of soil which must be added to a soil in order that the water layers most distant from the soil particle surface acquire the properties of free water. For sodium soil, the Liquid Limit is much higher, there is a sharp increase in clay-size particles and corresponding decrease of silt-size.

Potassium clay is an exception in so far as it possesses the highest Plastic Limit and the lowest moisture content for optimum compaction. Sodium soil showed greatest, and potassium salt the smallest, difference between Shrinkage and Liquid Limits. Coefficient of consolidation is smallest for sodium soil and largest for potassium soil.

Compressibility indicates the intensity of the forces holding the water films. At void-ratio 1.1, we have $Na > H > Mg > Ca > K = Nat$; at void-ratio 1.5, $Na > Ca > Mg > Nat > K$. The great difference between the effect of Na-, and K- is impressive.

Sodium soil suffers a large decrease in volume of water as loads are applied. Calcium soil has the least amount of total volume change: this indicates that the water films around the calcium soil particles are compact: the small increases of moisture content during reduction of pressure indicate small attraction for additional water.

Winterkorn, H. F., "Progress in Research on the Improvement of Soil Properties by the Use of Chemical Admixtures," Proc., Montana Nat. Bituminous Conf., 124, (1938).

Water-affinity is not for all soils directly proportional to the number of ions present, even if they are of the same kind, but this affinity depends also on the geometric and sterometric form of the surface with which the ions are connected (a fact explained by electrostatic considerations).

Surface-tension type of cohesion is the only one present in all soil materials from gravel to clay, as long as these materials possess only short range adsorption forces. Of course, the amount of cohesion depends on the number of connecting films and their radii of curvature (extremely small in case of plate-shaped fine particles). Maximum thickness of adsorption film also changes with shape of particle.

Maximum thickness of adsorbed water film on soil particles is a function of the charge, type and amount of exchangeable ions and of geometric structure of the mineral surface. Smallest thickness is obtained with convex and non-uniformly charged surface, the largest with a uniformly charged plane surface.

For plate-shaped particles: 1) marked uniform charge with extended ionic atmosphere of equal signs tends to increase the thickness of the water film and cause repulsion of the particles. At very low water content this decreases cohesion, while at high water content a pseudo-cohesion may be apparent because of establishment of certain structure (thixotropy). 2) A non-uniform charge with non-uniform ionic atmosphere can link two particles together by means of electric chains, starting at one point of one surface and leading over water dipoles and ions to an opposite charge of the opposite micelle: this leads to greatest cohesional properties.

Effects of Salt Treatment:- 1) Adsorption of ionic constituents of the salts on the soil particles and changing of their surface-chemical character. This effect is specific for the different ions. 2) Increase of surface tension of soil moisture, therefore, increase of "surface tension cohesion." 3) Equalization of water content by deliquescence, hygroscopicity, and water-retention property. 4) Decrease of volume change in drying, owing to crystallization of the salt. 5) Decrease of swelling capacity of soil due to presence of electrolyte in soil moisture. 6) Increase of solubility in electrolyte solution (e.g., calcium carbonate in sodium chloride); and possibility of recrystallization of this material with a specific cementing action.

Few Remarks on Fundamentals of Adhesion Problem:- 1) Adherence of one substance to another, or the adsorption of one substance by another, can be due to forces of non-polar, polar and intermediate type. 2) Polar adsorption is connected with larger amount of energy and will take place preferentially if both types are possible. 3) Special case of polar adsorption is the formation, at the interface of water and oil, insoluble compounds by constituents of the adsorbents and adsorbates. 4) With bitumens containing polar constituents, such as asphaltic acids, anhydrides and resins, and the minerals generally, consisting of ionic lattices with more or less marked polar character, polar adsorption should be expected to play a major role. 5) The adhesion of a bitumen to mineral surfaces can be changed with the help of inorganic and organic primers of a polar nature. 6) Primers which develop cementing films appear to be preferable to those which develop lubricating films, if it is desired that the cement introduce as much cohesive stability as possible.

Winterkorn, H. F., "Surface-Chemical Factors Influencing the Engineering Properties of Soils," (Abstract) Highway Research Board, 16, 293 (1936).

The test data showed that the physical character of natural soils especially as pertaining to stability at varying moisture contents can be changed to a great extent by a change of the adsorbed ions. Order of activity of cations:- sodium 8; aluminum 5; iron 0; magnesium 3; calcium 0; barium 2; hydrogen 3; potassium 2.

Stabilization of a soil without addition of aggregate implies a reduction of the water affinity and a cementing together of the soil grains. Permanent reduction of the water affinity can only be procured by chemical means, that is, by the exchange of bases for those that can become part of the crystal lattice of the soil mineral, thereby changing the surface properties of the soil, by substances which form insoluble compounds with the available valencies of di- or poly-valent ions on the surface of the soil grain, and by resin forming organic compounds which undergo exchange adsorption as a result of their basic nature and which are afterwards condensed to resins by the addition of other substances. For cements in situ, one liquid reagent should wet the mineral, the other help form a water insoluble compound.

If a clay is lateritic, as the moisture evaporates cohesion increases to a certain point, but when the moisture is completely evaporated there is nothing left which induces cohesion. With podsolic soil it is practically impossible to dry out the water entirely, therefore, in this case cohesion increases continuously with decreasing moisture content.

In the water adsorption and swelling of sodium-clay, two phenomena play a role. The first is the hydratation of the sodium ions (and perhaps satisfaction of some "rest" valencies of the mineral surface by adsorption of the water dipoles); and the second is the osmotic or kinetic effect which causes the ions to migrate as far from the mineral surface as the electrostatic attraction permits. Hydratation is connected with definite amount of heat of wetting. The energy involved in osmotic swelling depends on the activities of the ions around the soil particles and those in the swelling liquid. If the outside pressure plus the mechanical resistance to entrance of water equals the osmotic pressure around the soil particle, the soil will stop swelling.

Baral, Leon, "Preparation and Properties of Some Organo-Bentonite Compounds," M.S. Thesis, M. I. T., 1939.

This thesis investigates the production of organo-dispersions of bentonite using tricresyl phosphate, trimethyl benzyl ammonium hydroxide, diphenylamine, and cationic soaps as reagents. It was found that the reaction product of bentonite with cationic soaps was hydrophobic and organophilic. Self-supporting, coherent films made from the organo-dispersions exhibit the same structure as films made from water dispersions of bentonite but were not affected by water and were more flexible than the latter.

Danenberg, Eli M., "The Waterproofing Action of Lead Acetate upon Bentonite Films," M.S. Thesis, M. I. T., 1940.

The purpose of this thesis was to study the mechanism of the waterproofing action of lead acetate on bentonite films for use as di-electric material and for electrical insulation. From experimental results, it seems that most of the lead picked up by the films exist as absorbed basic lead acetate which is important in treating a moisture resistant film. This absorbed lead acetate seems to exert some kind of bonding strength between the clay particles, thus increasing the strength of the film; and further the capillaries and pores are filled up by the basic lead acetate causing a decrease in the available free surface for water absorption.

Neuman, Geza E., "A Study of the Polymers of the Salts of Acrylic Acid and the Combination of These Salts with Bentonite," S.B. Thesis, M. I. T., 1942.

The purpose of this thesis was to investigate the possibility of using the polymer of the salts of polymerizable carboxylic acids and the combination of these salts with base-exchangeable materials such as bentonite, as electrical insulators. Certain salts of acrylic acid were used and their polymers investigated. Lead acrylate proved the most successful, obtaining the desired properties of being stable at fairly elevated temperatures and also water stable.

Neuman, Geza E., "A Study of the Reactions of Lead Salts With Bentonite," S.M. Thesis, M. I. T., 1943.

This thesis investigates the reaction of lead salts with bentonite along five different lines: by varying the concentrations of lead acetate and lead nitrate solutions, it was found that at low concentrations the sorption of lead nitrate was higher than that from lead acetate. At high concentrations, the sorption from lead nitrate solutions was lower than that from lead acetate solutions; by varying the concentrations of mixtures of lead acetate and lead nitrate, the sorption was higher than the sorption from the individual solutions; for dry bentonite, the sorption is directly proportional to the milli-equivalents of lead salt in solution per gram of clay; bentonite gels sorb more strongly than dry bentonite clay; the viscosity of lead-salt-bentonite systems decreases with increasing concentration and increasing sorption.

Chi Wen Nie, "Studies in Alkali-Silicones," Sc.D. Thesis, M. I. T., 1946.

This thesis investigates the silicone resins and the possibility of modifying the curing process and improving the heat resistance by the addition of alkalis.

Penney, M. F., "Studies in Esterified Clays," S.B. Thesis, M. I. T., 1947.

The purpose first in mind in this thesis was to investigate the "esterification" of a potassium clay with an unsaturated organic halide and the subsequent copolymerization of these clays with vinyl acetate, styrene, or some other similar compound. The side reactions which occurred during the synthesis predominated the reaction, thus a study of the extent to which these reactions took place was undertaken.

Bart, R. and Gusman, S. "A Study of the Esterification of Bentonite Clays," S.B. Thesis, M. I. T., 1946.

This thesis investigates the reaction of clay minerals with esterifying agents to produce organophilic clay esters.

Salzman, E. L., "The Coating of Clay Films," M.S. Thesis, M. I. T., 1947.

This thesis investigates the possibility of using potassium to shorten the period of curing of silicone resins and also to study the general effects of potassium on these resins and to use the treated resin on clay films.

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The page numbers following each reference indicate the page in the report where the full reference may be found.

Baral, Leon
"Preparation and Properties of Some Organo-Bentonite Compounds," page 142.

Bart, R. and Gusman, S.
"A Study of the Esterification of Bentonite Clays," page 144.

Baver and Horner
"Water Content of Soil Colloids as Related to Their Chemical Composition," page 137.

Chi Wen Nie
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"The Chemical Nature of Clays," page 122.

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"The Absorption of Proteins by Montmorillonitic Clays and Its Effect on Base Exchange Capacity," page 130.

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"A Study of the Polymers of the Salts of Acrylic Acid and The Combination of These Salts with Bentonite," page 143.

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"Physical Characteristics of Soils: VI, Influence of Clay, Exchangeable Bases, and Hygroscopic Moisture on Soil Cohesion," page 129.

Rapp, P. and Mizroch, J.
"Effect of the Chemical Properties of Soil Fines on the Performance of Soil-Aggregate Mixtures," page 138.

Russell, E. W.
"The Interaction of Clay with Water and Organic Liquids as Measured by Specific-Volume Changes and Its Relation to the Phenomena of Crumb Formation in Soils," page 134.

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"The Coating of Clay Films," page 144.

Sideri, D. I.
"On the Formation of Structure in Soil: II, Synthesis of Aggregates; on the Bonds Uniting Clay with Sand and Clay with Humus," page 131.

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"Effect of Exchangeable Cations on Hydrophilic Nature of Kaolin and Bentonite," page 132.

Whittaker, H.
"Effects of Particle Size on Plasticity of Kaolinite," page 127.

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PART III BIBLIOGRAPHY

EXPLANATION OF DESIGNATIONS FOR REFERENCES

The first letter refers to the subject classification.

The following two numbers indicate the year of publication.

The number after the dash identifies sequentially the reference for a particular year.

Example - F38-2: the second reference listed in the bibliography for the year 1938 on the subject of sodium silicate stabilization.

A. Calcium Chloride

A29-1 Strahan, C. M.
"A Study of Gravel, Topsoil and Sand-Clay Roads in Georgia," Public Roads, Vol. 10, No. 7, 1929.
Can be considered fundamental work on stabilization establishing for first time the relationship between gradation and quality of sand-clay roads.

A29-2 Tarasov, D. I.
"Can a Water Extract Serve as an Index to Characterize the Degree of Salt Treatment of Soils," Pochvovedenic, Vol. 24, No. 3-4, pp. 61-99, (in English pp. 99-101), 1929.
See Chemical Abstracts 25, p. 3110, 1931.

A30-1 Burton, V. R. and Benkelman, A. C.
"The Relation of Certain Frost Phenomena to the Subgrade," Proc., Highway Research Board, Vol. 10, 1930.
Data on subject of title supported by laboratory evidence.

A30-2 Mullis, I. B.
"Illustrations of Frost and Ice Phenomena," Public Roads, Vol. 11, No. 4, 1930.
Physical characteristics of ice formation in soils and how it is manifested in highways and soils.

A31-1 Benkelman, A. C. and Olmstead, F. R.
"A New Theory of Frost Heaving," Proc., Highway Research Board, Vol. 11, 1931.
Results indicate excessive heaving may occur in soils of any grading or texture providing sufficient water is present.

A32-1 Burggraf, Fred
"The Use of Calcium Chloride as a Dust Palliative," Proc., Highway Research Board, Vol. 12, 1932.
Recognition that use of calcium chloride as a dust palliative has definite effect on stability of road.

A32-2 Casagrande, A.
"Discussion on Frost Heaving," Proc., Highway Research Board, Vol. 12, 1932.
Differences in various theories of frost heaving are presented and conclusions of experiments are drawn.

A32-3 Stewart, L. C. and Collings, W. R.
"Discussion on the Use of Calcium Chloride as a Dust Palliative," Proc., Highway Research Board, Vol. 12, Part II, p. 45, 1932.

A33-1 Blomgren, E. E. and Kushing, J. W.
"Stabilizing Michigan Gravel Roads with Clay and Calcium Chloride," Public Works, Vol. 64, No. 12, 1933.
Method of construction described.

A33-2 Collings, W. R. and Stewart, L. C.
"Preparation and Maintenance of Stabilized Gravel Roads," Am. Road Builders' Assoc. Bull., No. 36, 1933.
General review of all phases of calcium chloride granular stabilization.

A33-3 Erlenmeyer, H.
"The Migration of Salts in Soil," Chemie der Erde, Vol. 8, pp. 317-320, 1933.
See Chemistry Abstracts 28, p. 1803, 1934.

A33-4 Hogentogler, C. A. Jr.
"Moisture-Film, Cured Macadams," Public Works, Vol. 64, No. 11, 1933.
Stabilized bases with calcium chloride, properly seasoned, afford good bases for macadam covering.

A33-5 Hogentogler, C. A. Jr.
"Stabilization of Low-Cost Roads by Calcium Chloride," Roads and Streets, Vol. 76, No. 10, 1933.
Considers physical aspects of what makes a stable soil mixture and why.

A33-6 Proctor, R. R.
"Fundamental Principles of Soil Compaction," Engineering News-Record, Vol. 111, Nos. 1, 10, 11, 12, 13, 1933.
Theory and practice of soil compaction.

A33-7 Traver, R. B. and Hicks, W. B.
"Gravel Type Stabilized Surfaces for Secondary Roads," Proc., Highway Research Board, Vol. 13, 1933.
Methods and materials of construction described in some detail.

A33-8 Warren, S. S.
"Stabilization of Traffic Bound Roads Through the Calcium Chloride Method," Better Highways, Vol. 16, No. 6, 1933.
Points out advantage of getting same bearing or incorporation of sufficient metal in road bed in one year or one spread as could take three to five years under ordinary gravel road maintenance procedure.

A33-9 "Improved Low Cost Soil and Gravel Roads," Dow Chemical Company, Midland, Michigan, 1933.

A33-10 "Soil Stabilization in Highway Construction Through Calcium Chloride," Public Works, Vol. 64, No. 6, 1933.
General report of all types of stabilization being done in various sections of the country.

A33-11 "Stabilizing Earth Roads," Engineering News-Record, Vol. 111, No. 19, 1933.
Short note of general type of work being carried on in Michigan and in Onondaga county, New York.

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Title explanatory.

A34-2 Belknap, Leon and Barr, John
"Stabilization of Resurfacing Gravel," Public Works, Vol. 65, No. 8, 1934.
Methods of construction described for this type of work in Oakland county, Michigan.

A34-3 Blessing, Olin D. and Smith, Don N.
"Stabilization and its Relation to Maintenance of Traffic-Bound Roads," Better Roads, Vol. 4, No. 6, 1934.
Explains purpose of stabilization and its usual applications.

A34-4 Collings, W. R. and Stewart, L. C.
"Stabilized Soil-Bound Surfaces," Engineering News-Record, May 24, June 7, 14, and 21, 1934.
Complete series of articles on all phases of use of calcium chloride in granular stabilization.

A34-5 Del French, R. Prof.
"Soil Concretes, Performances and Possibilities," Canadian Engineer, Vol. 67, No. 12, 1934.
General review of principles of stabilization.

A34-6 Dow, W. O.
"Stabilization of Gravel Roads by Use of Calcium Chloride," Twentieth Ann. Road School, Purdue University, 1934.
Brief account of project in Indiana.

A34-7 Eno, F. H.
"New Application of Old Principle," Ohio State University Engineering Experiment Station News, Vol. 6, No. 1, Part I, 1934.
Refers to Strahan's work in Georgia. Note that calcium chloride stabilized road is being tested in Ohio.

A34-8 McClain, C. W.
"Stabilization of Gravel Roads by Use of Calcium Chloride," Twentieth Ann. Road School, Purdue University, 1934.
Brief account of project in Indiana.

A34-9 Miller, H. H. and Smith, Don N.
"Methods for Prevention of Road Failure Due to Frost," Roads and Streets, Vol. 77, No. 6, 1934.
Two treatments which have successfully eliminated frost failures in roads.

A34-10 Tiney, B. C.
"Soil Stabilization Insures Good Low-Cost Roads," Highway Magazine, Vol. 25, 1934.
Utilization of fine material in gravel, construction, and maintenance of gravel roads cost $100 to $400 per mile.

A34-11 Tyler, P. M.
"Calcium Chloride," U.S. Bureau of Mines, Information Circular 6781, 1934.
Nature, manufacture, occurrence, and properties of calcium chloride.

A34-12 Warren, S. S.
"Principles of Road Stabilization," Highway Topics, Vol. 11, No. 8, 1934.
General review of practice of soil stabilization.

A34-13 "Indiana Stabilizes Many Miles of Gravel-Surfaced State Highways," Outdoor Indiana, Vol. 1, No. 7, 1934.
More than 250 miles of gravel surfaced roads being treated.

A34-14 "Ohio Engineers View Stabilized Roads in Oakland County," Michigan Roads and Airports, Vol. 31, No. 21, 1934.
Announcement of visits of engineers to project.

A34-15 "Producer Makes Special Mixture for Calcium Chloride Treated Road Surfaces," Rock Products, Vol. 37, No. 6, 1934
Title explanatory.

A34-16 "State Tests New Type Road Surface," Minnesota Highway News, July 25, 1934.
Note that calcium chloride stabilized roads are being constructed and tested in Minnesota.

A35-1 Barr, John H.
"Stabilized Surfaces in Oakland County," Twenty-first Ann. Highway Conference, University of Michigan, 1935.
Description of experiences in Oakland county, Michigan using both plant and road mix methods of preparing calcium chloride stabilized materials.

A35-2 Barr, John H.
"Stabilized Surfaces in Oakland County," Michigan Roads and Construction, Vol. 32, No. 11, 1935.
Complete descriptions of methods of construction, costs, and findings on one project.

A35-3 Barr, John H. and Sours, H. G.
"Low-Cost Road Building, A Symposium," Engineering News-Record, Vol. 114, No. 26, 1935.
Accounts of experience and practice condensed from recent papers presented at meetings of road builders covering federal standards, farm service, oil mix, stabilized soil, and tar-retread.

A35-4 Burggraf, F.
"Importance of Crown on Calcium Chloride Stabilized Roads," Calcium Chloride Assoc. Bull., No. 23, 1935.
Recommendations for type of crown based on observations and measurements of many roads in service.

A35-5 Burggraf, F.
"Progress in Road Stabilization by Use of Calcium Chloride," Roads and Streets, Vol. 78, No. 4, 1935.
Developments in road stabilization such as construction, specifications, design, and maintenance.

A35-6 Chambers, Mark
"Improving City Streets Through Low-Cost Stabilization," American City, Vol. 50, No. 7, 1935.
Soil tests of existing surfaces revealed lack of binder material and some gravel in earth surfaces. Treatments described.

A35-7 Dow, W. O.
"Maintenance of Stabilized Gravel Roads," Michigan Roads and Construction, Vol. 32, No. 42, 1935.
Maintenance is as important as construction. Most important factor is time. Practice described.

A35-8 Dow, W. O.
"Notes on the Maintenance of Stabilized Gravel Roads," Better Roads, Vol. 5, No. 5, 1935.
Time of repair is critical. Methods described. Breakdown of costs.

A35-9 Flanders, J. D.
"Resurfacing Gravel or Stone Roads in Townships," Canadian Engineer, Vol. 68, No. 19, 1935.
Results and conclusions of experiences with stabilizations in Ohio. Methods of construction described.

A35-10 Glover, V. L.
"Practical Soil Stabilization," Twenty-second Ann. Conference on Highway Engineering, University of Illinois, 1935.
General review of field of stabilization.

A35-11 Hathaway, C. M.
"Stabilized Gravel Roads, Theory and Practice," Twenty-second Ann. Conference on Highway Engineering, University of Illinois, 1935.
Title explanatory.

A35-12 Hogentogler, C. A.
"Practical Soil Stabilization," Twenty-second Ann. Conference on Highway Engineering, University of Illinois, 1935.
Discussion of the physical properties of soils concerned with stabilization.

A35-13 Hogentogler, C. A.
"Soil Stabilization," Proc., Eleventh Ann. Convention Assoc. of Highway Officials of the North Atlantic States, 1935.
General discussion on subject utilizing physical-chemical relationships of soils.

A35-14 Huber, Jr. and Dick, M.
"Stabilized Gravel as Base Course for Bituminous Surfacing," Public Works, Vol. 66, No. 9, 1935.
Description of work in Washtenaw county, Michigan, in which stabilized gravel road was constructed, maintained for one year, and then a thin bituminous coating applied. Very satisfactory results.

A35-15 Knight, J. A.
"Stage Stabilization of Gravel Roads," Canadian Engineer, Vol. 69, No. 27, 1935.
Maintenance of gravel roads should be considered as progressive step toward the goal of a stabilized gravel road. Stages necessary for this development are described.

A35-16 Linzell, S. O.
"Stabilized Roads, Practical, Simple and Economical," Highway Magazine, Vol. 26, p. 209, 1935.
General description of work in Morrow county, Ohio.

A35-17 Miller, R. W.
"Cost of Building Stabilized Roads," American City, Vol. 50, No. 2, 1935.
Detailed costs of two projects in Minnesota presented. Costs vary with thickness of mat, cost of materials, etc.

A35-18 Patterson, T. R.
"Huron County's (Michigan) Experience in Stabilizing Gravel Roads," Canadian Engineer, Vol. 69, No. 13, 1935.
Title explanatory.

A35-19 Reppel, J. W.
"Experimental Stabilization in Ohio," Roads and Streets, Vol. 78, No. 12, 1935.
Title explanatory.

A35-20 Sours, H. G.
"Progress in Stabilized Traffic-Bound Roads," Better Roads, Vol. 5, No. 4, 1935.
General review of stabilization. Two methods of application of calcium chloride described; surface application and integral mix.

A35-21 Sours, H. G.
"Stabilized Roads a Real Job," Contractors and Engineers Monthly, Vol. 30, No. 5, 1935.
Results and conclusions of experiences with stabilization in Ohio. Methods of construction described.

A35-22 Stewart, L. C. and White, S. J.
"Premixed Stabilized Soil for Road Surfaces," Engineering News-Record, Vol. 115, No. 12, 1935.
Details, including design of demonstration plant built for producing stabilized gravel.

A35-23 "Calcium Chloride Stabilization," Report of Special Committee, Highway Research Board, 1935.
Complete report on calcium chloride stabilization.

A35-24 "Maintenance of Calcium Chloride Stabilized Roads," Calcium Chloride Assoc. Bull., No. 18, 1935.
Title explanatory.

A35-25 "Outline for Low-Cost Road Improvement Through Stabilization With Binder Soil and Calcium Chloride," Calcium Chloride Assoc. Bull., No. 22, 1935.
Title explanatory.

A35-26 "Stabilization of Ontario Roads with Calcium Chloride," Canadian Engineer, Vol. 69, No. 11, 1935.
Impetus in interest caused by manufacture of calcium chloride at Amherstburg, Ontario. General description of construction work being carried out.

A35-27 "Stabilized Roads in West Virginia," West Virginia Highways, January, 1935.
Report of use of stabilized gravel roads.

A36-1 Atkin, Bernard
"Gravel and Broken Stone Surfaces," Twenty-third Ann. Conf. on Highway Engineering, University of Illinois, 1936.
Value of calcium chloride use in stabilization recognized on all road sections built during past two years.

A36-2 Clemmer, H. F.
"Stabilization of Soils," Roads and Streets, Vol. 79, No. 12, 1936.
General review of principles of soil stabilization.

A36-3 Hogentogler, C. A., Jr.
"Essentials of Soil Compaction," Proc., Highway Research Board, Vol. 16, 1936.
Report largely concerned with principles of compaction, conditions of moisture, film thickness, and the effect of electrolytes in stabilized soils.

A36-4 Hogentogler, C. A. and Willis, E. A.
"Stabilized Soil Roads," Public Roads, Vol. 17, No. 3, 1936.
Discussion of the physical and chemical properties of soil involved in stabilization; effect of deliquescent chemicals described.

A36-5 Housel, W. S.
"Subgrade Stabilization," Twenty-second Ann. Highway Conf., University of Michigan, 1936.
In low cost surfaces such as stabilized roads it is difficult to demarcate between roadway structure and its foundation. Discussion on principles and methods.

A36-6 Hurst, E. G.
"Smoothing Stabilized Gravel for Asphalt Surfacing," Engineering News-Record, Vol. 116, No. 15, 1936.
Unique problem of one particular road and its preparation for asphalt surface.

A36-7 Lang, F. C.
"Stabilization of Soil and Gravel Roads," Convention Proc. American Road Builders Assoc., 1935-1936.
Review of methods used in construction of stabilized roads in Minnesota. Progress of stabilization is retarded by lack of proper equipment and insufficient knowledge as to proper construction and maintenance methods.

A36-8 Linzell, S. O.
"Stabilized Road Surfacing in Ohio," Roads and Streets, Vol. 79, No. 12, 1936.
Calcium chloride used in surface application only.

A36-9 Miller, R. W.
"Effect of Quality of Clay on Soil Mortars," Proc., Highway Research Board, Vol. 16, 1936.
Compaction and swell tests indicate that Plasticity Index limits of 4 to 12 for soil fines or minus 40 mesh material cover range usually encountered in various localities.

A36-10 Slater, F. A.
"Plant Production of Stabilized Mix," Canadian Engineer, Vol. 70, No. 15, 1936.
Production of stabilized gravel containing specified proportions of calcium chloride, clay, sand, and pea gravel described.

A36-11 Smith, A. R.
"Salt Stabilization of Highway Subgrades and Surfaces in Indiana," Twenty-third Annual Convention American Road Builders' Assoc., Cleveland, Ohio, January 20-24, 1936.

A36-12 Stewart, L. C.
"Design and Operation of Plants for Producing Stabilized Soil-Bound Road Material," Proc., Highway Research Board, Vol. 16, 1936.

A36-13 Tiney, B. C.
"Shoulder Stabilization," Roads and Streets, Vol. 79, No. 7, 1936.
Methods of construction of calcium chloride stabilized road shoulders. Central mixing plant suggested.

A36-14 Traver, R. B.
"Low-Cost Stabilized Road Construction," Canadian Engineer, Vol. 70, No. 8, 1936.
Methods of procedure and construction of stabilization in Onondaga county, New York, described in detail.

A36-15 Wagner, H. S.
"Patching Calcium Chloride Roads," Parks and Recreations, Vol. 20, No. 2, 1936.
Suggest expensive blading, planing, and reshaping can be eliminated or confined to once or twice a year by proper patching. Method described.

A36-16 Wilford, H. D.
"Stabilizing Gravel Roads in Victoria County," Canadian Engineer, Vol. 70, No. 8, 1936.
Report of construction.

A36-17 "Detroit Builds Soil Pavements," Calcium Chloride Assoc. News, August, 1936, p. 5.
Brief note of what is being done.

A36-18 "Detroit Plant Uses Crushed Slag to Make Stabilized Road Mixture," Pit and Quarry, Vol. 28, No. 8, 1936.
Title explanatory.

A36-19 "Michigan Gravel Firm Takes Advantage of Demand for Stabilized Road Material," Pit and Quarry, Vol. 29, No. 4, 1936.
Description of production of stabilized soil aggregate mixture.

A36-20 "Pioneer Gravel Equipment," Michigan Roads and Construction, Vol. 33, No. 2, 1936.
Description of a portable gravel clay stabilizer plant designed to work in conjunction with a crushed gravel plant and to prepare and mix materials for stabilization.

A36-21 "Plant Mixing Stabilized Aggregates for Low-Cost Roads," Calcium Chloride Assoc. Bull., No. 24, 1936.
Design of plant and details of mix for preparing plant mixed stabilized aggregate.

A36-22 "Solving Gravel-Road Maintenance Problems," Better Roads, Vol. 6, No. 8, 1936.
Reports of very satisfactory results by using calcium chloride and clay in maintenance.

A36-23 "Stabilized Road Construction in Minnesota," Earth Mover, Vol. 23, No. 10, 1936.
Use of three methods; road mixed by blading, machine mixed on road, and plant mixed for preparing stabilized material. Calcium chloride used in all.

A36-24 "Stabilized Soil Road Withstands Erosion," Roads and Streets, Vol. 79, No. 2, 1936.
Illustration showing calcium chloride stabilized road after torrential rain, near Vincennes, Indiana.

A36-25 "Stabilization for Street Improvement," Public Works, Vol. 67, No. 4, 1936.
Brief descriptions of street stabilization jobs in Lansing, Michigan; Ames, Iowa; and Detroit, Michigan. Both road and plant mix methods used.

A36-26 "State Highway Department Builds Test Stabilized Road," Pennsylvania Road Builder, Vol. 9, No. 9, 1936.
Limestone screenings, clay, and calcium chloride added to gravel road according to tests showing deficiencies.

A37-1 Allen, L. L.
"Road Stabilization," Proc., Am. Road Builders' Assoc., 1937.
In 1932, survey showed 13 states and District of Columbia had laboratories capable of performing soil classification tests. Two years later, 27 state highway departments were equipped. Reviews Minnesota experience.

A37-2 Baise, W. Vance
"North Carolina Stabilized Job Stands Winter Well," Contractors and Engineers Monthly, Vol. 34, No. 5, 1937.
Methods given that were used to construct 5.6 miles of calcium chloride stabilized road. Reported to be in good condition after winter.

A37-3 Best, V. E.
"Low-Cost Improvement of Streets," Pennsylvania Road Builder, Vol. 10, No. 11, 1937.
Street sections withstood winter without any repairs

A37-4 Brickler, A. R.
"Developments in Road Stabilization," Extension Series No. 38, Engineering Extension Dept., Purdue University, 1937.
Concerned with stabilized bases. Details on use of several methods of stabilization employing various mixes.

A37-5 Burggraf, F.
"Stabilization with Aggregates, Binder-Soil and Calcium Chloride," Proc., Am. Road Builders' Assoc., 1937.
General review article on all phases of subject.

A37-6 Clemmer, H. F.
"Developments in Municipal Road Surfaces," Canadian Engineer, Vol. 73, No. 14, 1937.
Maximum density utilizing existing sources of supply of materials is prime requisite of stabilized soil mix design. Review of practice in United States.

A37-7 Evans, W. E.
"Soil Stabilized Road Construction," Roads and Road Construction, Vol. 15, No. 176, 1937. (England).
General review of practice in United States.

A37-8 Hogentogler, C. A.
"The Physical Chemistry of Highway Subsoils," Twenty-third Ann. Highway Conf., University of Michigan, 1937.
General study of physical-chemical properties of soil and their influence in soil stabilization.

A37-9 Hogentogler, C. A.
"Soil Stabilization," Proc., Thirteenth Ann. Convention, Assoc. of Highway Officials of the North Atlantic States, 1937.
Review of principles of soil stabilization.

A37-10 Hogentogler, C. A. and Kelley, J. A.
"Role of Soil Binders and Aggregates in Soil Stabilization," Proc., Am. Road Builders' Assoc., 1937.
Whole theory of soil stabilization based on two facts: (1) all soil mixtures common for road usage are stable at some moisture content, (2) moisture in stable roads is more adhesive than free water and stability depends upon thickness of adsorbed moisture films.

A37-11 Knight, J. A.
"Surface Consolidation Method Produces the 'Costless' Road," Highway Topics, Vol. 14, No. 11, 1937.
In past, stages of construction were; dirt surfaces, gravel, black top, finally hard surface; now, gravel surface itself can be built in stages by method called "surface consolidation." Construction details given.

A37-12 Lang, F. C.
"Combating Frost and Drainage Problems," Twenty-third Ann. Road School, Purdue,University, 1937.
Report on mechanics of frost heaving and methods of combating problem.

A37-13 Lang, F. C.
"Methods of Soil Stabilization and Low-Cost Roads," Twenty-third Ann. Highway Conf., University of Michigan, 1937.
Stresses importance of good subgrade for all types of road. Methods described.

A37-14 McClain, C. W.
"Combating Frost and Drainage Problems," Twenty-third Ann. Road School, Purdue University, 1937.
General discussion of problem.

A37-15 Ranney, Arthur F.
"Stabilized Secondary Roads in Summit County, Ohio," Better Roads, Vol. 7, No. 11, 1937.
Brief account of experience in construction of 1.25 miles of construction in North Malden, Ontario.

A37-17 Stewart, L. C.
"Plant Mixed Materials and Pulverization of Clay," Proc., Am. Road Builders' Assoc., 1937.
Reviews entire field of plant mixed stabilizers; types of plants, construction of plants, mixers, etc.

A37-18 "Estimating Construction Costs for Road Stabilization," Public Works, Vol. 68, No. 7, 1937.
Charts presented showing costs of stabilization and new aggregate.

A37-19 "Low Cost Roads," Calcium Chloride Assoc. Bull., No. 25, 1937.

A37-20 "Outstanding Stabilized Road Built Under Contract," Highway Builder, Vol. 16, No. 5, 1937.
Previously most stabilization had been done by highway department. Contract work successful.

A37-21 "Stabilized Streets for a Housing Project," American City, Vol. 52, No. 2, 1937.
Short article briefly describing use of calcium chloride stabilized mixture in street construction of low cost housing project.

A37-22 "The Story of Calcium Chloride as a Road Binder," Part I - Introduction, Part II - History, Occurrence, Manufacture, and Utility, Part III - Deliquescence and Hygroscopic Properties, Part IV - Surface Tension and Vapor Pressure. Calcium Chloride Assoc. News, May-June, July-August, September-October, November-December, 1937.
Title explanatory.

A38-1 Ames, John H.
"Residential Street Improvement," American City, Vol. 53, No. 4, 1938.
Low cost methods required commensurate with traffic. Details of experience given.

A38-2 Bateman, L.
"Surface Consolidation," Better Roads, Vol. 8, No. 4, p. 24, 1938.

A38-3 Beskow, G.
"Prevention of Detrimental Frost Heave in Sweden," Proc., Highway Research Board, Vol. 18, Part II, 1938.
Title explanatory.

A38-4 Black, J. C.
"Production and Use of Stabilized Maintenance Material," Roads and Streets, Vol. 81, No. 6, 1938.
Clay and admixture mixed with gravel at plant and used in repair of shoulder ruts at edge of concrete.

A38-5 Burmister, D. M. Prof.
"The Grading-Density Relations of Granular Materials," Columbia University. Proc., Am. Soc. for Testing Materials, Vol. 38, Part II, 1938.
Title explanatory.

A38-6 Cormier, George J.
"Stabilized Roads," Proc., Am. Road Builders' Assoc., 1938.
Stabilization experiences in Brown county, Wisconsin.

A38-7 Downey, B. R.
"Sprinkling of Stabilized Roads Proves Success," Michigan Roads and Construction, Vol. 35, No. 31, 1938.
Sprinkling helps keep gravel trunk lines in good condition during summer.

A38-8 Hogentogler, C. A.
"Developments in Soil Stabilization," Proc., Am. Road Builders Assoc., 1938.

A38-9 Lieberman, Ernst
"Current Developments in Stabilized Gravel and Crushed Stone Roads," Fifth Ann. Mineral Industries Conf., State Geological Survey, Urbana, Illinois, Circ. No. 23, 1938.
Three applications of calcium chloride recommended; of 3/4 lb. per sq. yd. in May, July, and September.

A38-10 Tiney, B. C.
"Betterment in Maintenance by Partial Stabilization," Public Works, Vol. 69, No. 10, 1938.
Methods of surface consolidation described.

A38-11 Tiney, B. C.
"Important Details in Stabilization with Calcium Chloride," Public Works, Vol. 69, No. 1, 1938.
Trend of design of stabilized mixtures has been to reduce proportion of binder soil and thereby lower Plastic Index of mixture. Changes in practice developing

A38-12 Williams, A. M., Otto Hess, and Burridge, A. L.
"Many County Roads Stabilized with Calcium Chloride," Michigan Roads and Construction, Vol. 35, No. 42, 1938.
Comments of three county engineers all favorable to calcium chloride stabilization.

A38-13 Winn, H. F.
"Frost Action in Stabilized Soil Mixtures," Proc., Highway Research Board, Vol. 18, Part I, 1938.
Presentation of experimental data on the relation of frost action in stabilized soil mixtures to gradation of soil mixture, type and percentage of admixture, and moisture content at beginning of freezing period.

A38-14 "Building a Stabilized Gravel Road," Improvement Bulletin, Vol. 85, No. 8, 1938.
Stabilized gravel road built under contract. Methods given.

A38-15 "Consolidating Gravel County-Road Surfaces," Better Roads, Vol. 8, No. 5, 1938.
Michigan experiments on gravel road maintenance. General practice.

A38-16 "Consolidation of Roads with Calcium Chloride," Canadian Engineer, Vol. 74, No. 23, 1938.
Brief description of practice.

A38-17 "Pennsylvania Utilizes Local Materials in State-Wide Road Stabilization," Construction Methods and Equipment, Vol. 20, No. 3, 1938.
Testing laboratory has set up and written specifications for five general designs of mixtures. General construction methods.

A38-18 "Stabilized Base for Black Top Road on U. S. 10," Michigan Roads and Construction, Vol. 35, No. 23, 1938.
Base course is calcium chloride clay stabilized gravel mixed in plant as required by Michigan specifications.

A38-19 "The Stabilizing Effects of Calcium Chloride in Construction of Soil-Aggregate Bases and Wearing Courses," Calcium Chloride Assoc., Technical Bull., No. 134, 1938.

A38-20 "Surface Consolidation and Dustless Maintenance of Traffic-Bound Roads," Calcium Chloride Assoc., Bulletin No. 33, 1938.

A38-21 "Use of Calcium Chloride in Road Stabilization," "Symposium." Contributors: C.F. Briggs, F. Burggraf, B. R. Downey, J. Elleman, C.A. Hogentogler, Jr., J. A. Knight, and H.D. Wilford. Proc., Highway Research Board, Vol. 18, Part II, 1938.
Complete series of short articles on all phases of use of calcium chloride in stabilization.

A39-1 Brown, Victor J. and others
"Soil Stabilization," Gillette Publishing Co., 1939.
Reprinted from six 1938 issues of Roads and Streets. General principles of stabilization.

A39-2 Burggraf, F.
"Field Tests on Shearing Resistance," Proc., Highway Research Board, Vol. 19, 1939.
Tests with field shearing apparatus correlated with tests on calcium chloride stabilized road.

A39-3 Burggraf, F.
"Field Tests Reveal Calcium Chloride Increases Density and Structural Stability," Calcium Chloride Assoc. News, May-June, 1939.
Stabilized mixtures containing calcium chloride attain same degree of compaction with less than half as much rolling as untreated mixtures.

A39-4 Elleman, John H.
"Use of Calcium Chloride in Road Stabilization," Proc., Am. Road Builders' Assoc., 1939.
General article on review nature on use of calcium chloride in stabilization.

A39-5 Glasgow, Paul E.
"Good Surfaces from Cheap Local Gravel," Better Roads, Vol. 9, No. 11, 1939.
Utilization of cheap local gravel in calcium chloride stabilization.

A39-6 Halbfass, F. P. G.
"Stabilized Gravel Roads in Muscatine County, Iowa," Public Works, Vol. 7, No. 11, 1939.
Description of construction.

A39-7 Miller, Herman
"Stabilization, Surface Consolidation, and Dust Laying." Dowflakes, Vol. 1, No. 1, 1939.
Definitions of different types of stabilization and use of calcium chloride in both.

A39-8 Mills, E. L.
"Slag and Calcium Chloride Give Good Base for Black Top Surface," Public Works, Vol. 70, No. 6, 1939.
Main street of Deersville, Ohio, prepared for black top surface by calcium chloride stabilization.

A39-9 Swinton, R. S.
"Gravel-Road Surface Wear Measured in Michigan Investigations," Better Roads, Vol. 9, No. 1, 1939.
Under closely controlled conditions calcium chloride stabilized road showed 36 per cent wear compared to 100 per cent for an untreated gravel road.

A39-10 Traver, R. B.
"Stabilization by Use of Chemicals," Twenty-fifth Ann. Road School, Purdue University, 1939.
General review of field of stabilization.

A39-11 Tremayne, J. E.
"Calcium Chloride Road Construction," Canadian Engineer, Vol. 76, No. 2, 1939.
An outline of a practical and economical method of providing adequate surfaces for gravel road traffic.

A39-12 Willis, E. A. and Carpenter, C. A.
"Studies of Water-Retentive Chemicals as Admixtures with Nonplastic Road Building Materials," Public Roads, Vol. 20, No. 9, 1939.
Article on use of outdoor circular track to determine the effect of chemicals including calcium chloride on non-plastic granular mixtures both with and without a thin bituminous surface treatment.

A39-13 "Calcium Chloride for Streets in Belgian Congo," American City, Vol. 54, No. 5, 1939.
Brief report on use of calcium chloride for stabilizing streets.

A39-14 "Calcium Chloride in Construction," Engineering Journal, Vol. 22, No. 8, 1939.
Physical and chemical properties of calcium chloride and general methods of use in construction.

A39-15 "Consolidation of Gravel Roads," Surveyor (England), Vol. 96, No. 2477, 1939.
Standard procedures of calcium chloride stabilization in Quebec, Canada.

A39-16 "Economics of Stabilization with Calcium Chloride," "Symposium" Contributors: W.F. Abercrombie, A.L. Brown, F.L. Brown, H.F. Clemmer, G. Farnsworth, P. Glasgow, J.E. Moreland, and R.M. Whitton. Proc., Highway Research Board, Vol. 19, 1939.
Symposium on subject of title.

A39-17 "Production of Stabilized Gravel," Construction Methods and Equipment, Vol. 21, No. 2, 1939.
Note that stabilized mixture is being produced at rate of 90 cu. yd. per hour in plant.

A40-1 Belcher, McAlpin and Woods
"Current Practices in Stabilization," Purdue Conference, p. 419, 1940.

A40-2 Burggraf, F.
"Field Tests and Their Application to the Design of Stabilized Soil Roads," Proc., Am. Road Builders' Assoc., 1940.
Describes apparatus designed to test resistance to shear of components making up a road structure. Results of tests given.

A40-3 Elleman, J. H.
"Calcium Chloride Surface Consolidated Roads," Proc., Highway Research Board, Vol. 20, 1940.
Description of construction and maintenance of calcium chloride stabilized roads.

A40-4 Glasgow, Paul E.
"Stabilized Base for County Roads," Contractors and Engineers Monthly, Vol. 37, No. 1, 1940.
Procedure described in converting traffic bound surfaces or more heavily traveled roads into low cost, more stable surfaces in Wayne county, Ohio.

A40-5 Hogentogler, C. A.
"Soil Stabilization," Twenty-sixth Ann. Highway Conf., University of Michigan, 1940.
General discussion on volume changes in soils with moisture.

A40-6 Olmstead, F. R.
"Plant Control of Stabilized Mixtures," Proc., Am. Road Builders' Assoc., 1940.
Complete article on use of plant mix materials in Michigan.

A40-7 Olmstead, F. R.
"Plant Mix Stabilized Aggregate for the Michigan Secondary Road System," Better Roads, Vol. 10, No. 1, January, 1940.
Reviews the methods used to assure the uniform production of stabilized materials.

A40-8 Osterberg, J. O.
"A Survey of the Frost-Heaving Problem," Civil Engineering, Vol. 10, No. 2, 1940.
Review on mechanics of frost heaving.

A40-9 Rapp, Paul and Mizroch, Jacob
"Effect of the Chemical Properties of Soil Fines on the Performance of Soil-Aggregate Mixtures," Public Roads, Vol. 21, No. 10, 1940.
Data presented showing the relationship of chemical properties to physical properties and the behavior of roads.

A40-10 Ravn, H. H.
"Frost Damage on Roads," (Denmark) Highway Research Abstracts No. 71, 1940. Highway Research Board.
Types of frost damage described and methods of prevention presented.

A40-11 Root, W. H.
"Evolution of Low-Cost Roads," Better Roads, Vol. 10, No. 6, 1940.
Procedure in stabilizing loose gravel surfaces.

A40-12 Schaub, J. G.
"Gravel Bases for Bituminous Surface," Twenty-sixth Ann. Highway Conference, University of Michigan, 1940.
Michigan adopted practice of placing bituminous surface treatment on newly laid gravel bases or reconstructed old gravel roads. Procedures presented in construction of calcium chloride stabilized bases.

A40-13 Willis, E. A. and Smith, P. C.
"Chemical Treatment of Chert-Gravels for Use in Base-Course Construction," Public Roads, Vol. 21, No. 4, 1940.
The use of admixtures to chert gravels for base course construction tested by means of a laboratory circular track.

A40-14 Woolley, W. R.
"Fundamentals of Road and Subgrade Stabilization," Twenty-sixth Ann. Road School, Purdue University, 1940.
Title explanatory.

A41-1 Belcher, D. J.
"A Field Investigation of Low-Cost Stabilized Roads," Engineering Bulletin of Purdue University, Research Series, No. 81, Vol. 25, No. 2a, 1941.
Field tests supported by laboratory experiments involving use of several types of admixtures. Methods of construction presented.

A41-2 Downey, B. R.
"Soil Control in Consolidated Maintenance," Proc., Highway Research Board, Vol. 21, 1941.
Detailed procedures presented of actual construction and maintenance of this type of road. Stress laid on systematic organization.

A41-3 Halbfass, F. P. G.
"Results and Experiences with 'Low-Cost Roads' Construction Types," Public Works, New York, Vol. 72, No. 7, pp. 17 and 38, 1941.

A41-4 Hathaway, C. M.
"Developments in the Construction Field," Twenty-eighth Ann. Conference on Highway Engineering, University of Illinois, 1941.
Title explanatory.

A41-5 Hemmerick, George
"Calcium Chloride for Base Stabilization," Canadian Engineer, Vol. 79, No. 3, 1941.
Brief review of general practice.

A41-6 Nunn, E. H.
"A Rational Approach to the Secondary Road Problem," Crushed Stone Journal, Vol. 16, No. 3, 1941.
Procedure based on soil tests, conditions in temperature, humidity, and traffic.

A41-7 Schmitt, John S.
"Stearns County Experiments with Calcium Chloride Stabilization," Public Works, Vol. 72, No. 6, 1941.
General account of practice.

A41-8 Smith, A. Jr.
"Road Base Construction of Graded Aggregate in Wisconsin," Dowflakes, Vol. 2, No. 6, 1941.
General account of work in Wisconsin.

A41-9 Van Auken, W. T.
"Surface Stabilization in DeKalb County, Indiana," Proc., Twenty-seventh Ann. Road School, Purdue University, 1941.
General account of treatment.

A41-10 "Soil Aggregate Stabilization and Use of Calcium Chloride for Military Roads and Airport Runways," Calcium Chloride Assoc., Bulletin No. 26, p. 24, 1941.

A42-1 Amstutz, M. E.
"Stabilized Bases Mixed at Pit," Better Roads, Vol. 12, No. 9, 1942.
Binder soil added to gravel at pit before going to be crushed. Method of construction given.

A42-2 Casagrande, L.
"What Has the Frost Damage of Last Year Taught Us?" (Germany) Highway Research Abstracts, No. 86, 1942, Highway Research Board.
Title explanatory.

A42-3 Davis D. S,
"Calcium Chloride Nomographs," Industrial and Engineering Chem., Industrial Edition, Vol. 34, No. 1, 1942.
Nomographs presented for calculation of properties of calcium chloride solutions by hydrometric methods of analysis.

A42-4 Griffin, L. B.
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D39-4 Gray, P. O., and Stone, I.
U.S. Patent No. 2,159,986, patented May 30, 1939.
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D39-5 Halvorsen, A. L.
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U.S. Patent No. 2,158,025, patented May 9, 1939.
Details of process for solidifying soils.

D39-21 van Hulst, Jan
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A process for making impervious loose or porous subsoil layers by injecting first an aqueous dispersion of bitumen into the mass and then introducing an impermeabilizing agent.

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D39-23 Winterkorn, H. F.
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D39-24 Zapata, J.
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D39-25 "Societe de recherches et de perfectionnements industriels," German Patent No. 674,813, April 22, 1939.
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D40-2 Buntru, A. and Komadina, R.
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D40-9 Ewers, N.
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"A Practical Laboratory Method of Analysing for the Constituents of Bitumen," Proc., Assoc. Asphalt Paving Tech., Vol. 12, p. 87, 1940.

D40-13 Heine, R. M.
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D40-18 Knight, B. H.
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