

## UNITED STATES PATENT OFFICE

2,651,619

## STABILIZATION OF SOILS

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Application January 25, 1951, Serial No. 207,723

18 Claims. (Cl. 260-41)

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The present invention relates to methods for stabilizing soils and are more specifically to the solidification of natural soils by chemical treatment.

The desirability of stabilizing soils by chemical treatment has long been recognized, and many attempts have been made to discover operative techniques and materials. Thus, much work has been done with chlorides, particularly calcium chloride, with tars and asphalts, Portland cement, and various natural and synthetic resins. Many of such treatments provide some degree of waterproofing, in certain types of soils, but fail to add appreciable strength.

The problem of soil stabilization is particularly acute in the case of fine-grained clay soils, where the effect of water is so marked. Such soils may lose substantially all their shear strength when they become very wet, so as to be impassable for vehicles. Existing treatments become relatively ineffective as the size of the soil particles decreases, with the result that the fine-grained clay soils, which are the type for which stabilization is most needed, have heretofore not been successfully treated.

Another difficulty with existing treatments is that they for the most part require a strong base or foundation to carry the load, since the treated soil has but little flexibility and tensile strength. Even in the case of treatments such as soil-cement, where the resulting product is rigid, a proper foundation is needed to prevent cracking under load.

It is therefore one of the main objects of the invention to provide a soil treating process by which the structural properties of naturally occurring soils may be substantially improved. More specifically, it is an object of the invention to provide a process for stabilizing soils of various types and particularly the fine grained clay type soils, so as to provide for the passage of vehicles thereover without the need for a prepared base or foundation.

It is likewise an object of the invention to provide a treatment which makes possible the formation of soil structures such as walls, blocks, dams, bankings and the like, of substantial strength, relatively impermeable, and able to withstand the effects of water.

A further object of the invention is to provide a soil treatment that requires a relatively small quantity of treating material in proportion to the soil being treated.

Still another object of the invention is to provide a treating process that is effective to treat

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in situ naturally occurring soils having various water contents, so as to impart to such soils appreciable strength both in shear and in tension, with properties substantially unaffected by water once treatment has been effected.

In accordance with these and other objects, one of the features of the invention involves the provision of a soil treating method and materials therefor wherein the treating materials may readily be incorporated in naturally occurring soils and polymerization thereafter brought about, without the application of heat or pressure, to yield a treated product having substantial tensile strength and relatively unaffected by water.

More specifically, the treatment involves the incorporation in the soil of a chemical in the form of a monomer capable not only of being solidified by polymerization, but of causing the soil particles to enter into the structure by effective bonds or links, rather than embodying the soil merely as an inert filler.

As more fully set forth hereinafter, a monomer is employed which will ion exchange with a base-exchangeable soil, or will by other means provide an effective bond in the case of soils which exhibit no base exchange properties, which monomer may thereafter be polymerized to form long chain polymers in which soil particles are interwoven and attached to strong flexible polymer chains. Though the monomer is water soluble, the polymer which is formed is insoluble in water, with the result that the effects of water are greatly minimized and the treated soil or soil product is rendered strong and durable.

The treatment has been found to be applicable to a wide variety of soils, and permits the building of roadways such as secondary or temporary highways, airport runways and the like with a minimum of preparation and in a short period of time. The treatment is likewise applicable to the fabrication of soil structures as dams and bankings, walls and foundations, as well as to products such as blocks, all having substantial strength and relatively unaffected by water.

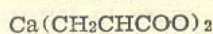
In the drawings, to which reference may be made in conjunction with the accompanying description, Figs. 1, 2, and 3 represent diagrammatically the steps of ionization, base exchange, and polymerization that go to make up the solidification reaction; Fig. 4 is a representation of the overall resulting soil-polymer structure; and Fig. 5 is a diagrammatic showing of the man-

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ner in which the treated soil provides effective load-carrying properties.

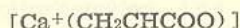
As has already been indicated, the present invention is concerned with treatment of the soil by a chemical that provides a two-fold function, that of base exchanging with the soil, or in other fashion bonding or entering into surface attraction relation to the soil particles, after which the chemical is polymerized within the soil to form a coherent structure. The treating material must therefore possess rather special properties, in order for the reaction to proceed successfully, over the wide range of soil types and conditions encountered with naturally occurring soils.

In carrying out the soil treating process of the present invention, we have found that calcium acrylate is particularly desirable as a monomer and it will be used as an example throughout the following description. Calcium acrylate is an organic salt having the formula



and can be made by mixing calcium carbonate with acrylic acid.

Upon addition of calcium acrylate to the soil, there occurs a dissociation of the calcium acrylate in the water contained in the soil, resulting in the formation, among other ions, of a positively charged calcium acrylate ion,



This ion can become attached to a soil particle in an exchange reaction.

It is well known that most soil particles, particularly the clays, have an excess of negative charge on their surface and that a base-exchangeable cation such as sodium is associated with the particle through an ionic bond. Therefore, the dissociation of calcium acrylate according to the above reaction is accompanied by a base exchange reaction in which the singly ionized calcium acrylate ions  $[\text{Ca}^+(\text{CH}_2\text{CHCOO})]$  can replace cations, such as sodium ( $\text{Na}^+$ ), associated with the soil particles. This reaction is pictured schematically in Figs. 1 and 2, the initial state of the soil and calcium acrylate mixture being shown in Fig. 1, and the exchange step in Fig. 2. Although the coarser soil particles, such as sand, are not usually considered to be capable of base exchange, on the basis of present knowledge it is believed that these particles have enough surface attraction due to the discontinuity in the crystal structure on the surface to provide some degree of bonding with cations.

The role of the base exchange reaction is to bring the soil particles into close association with the monomer so that, upon polymerization, the soil particles become an integral part of the polymer structure. The base exchange reaction alone, as above described, does not result in an increase in the strength of a soil but instead generally causes an appreciable decrease in the shear strength of the soil. However, after polymerization the bond formed by the base exchange reaction serves to hold the soil particles in the soil-polymer structure, thus adding appreciably to the strength of the final product.

After the soil has been treated with calcium acrylate and the above-mentioned base exchange has taken place, the soil monomer mixture is polymerized. This polymerization is effected at normal outdoor temperatures and pressures through the use of suitable catalysts comprising both an oxidizing agent and a reducing agent.

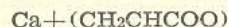
Such catalysts are termed reduction-oxidation, or redox, catalysts.

The final soil product after polymerization is an extremely complex structure and cannot be presented by a simple picture. Fig. 3 shows in elementary fashion the linking to the soil through the calcium ions, while the structure shown in Fig. 4 illustrates in overall fashion the complex long chain and cross-linked relations that are believed to exist in the soil structure between the soil particles and the treating chemicals.

It will be noted from Fig. 4 that each soil particle is attached to the polymer chain through an ionic bond with the calcium atom in the calcium acrylate polymer. Actually a given soil particle may have a number of such bonds with calcium atoms each tied to a given link in the polymer chain. The sodium, or other cation, which has been released from the soil particles in the base exchange, is structurally attached to the polymer chain as a sodium acrylate link. Such portion of the calcium acrylate as does not become attached to soil particles through base exchange is available to form cross-links in the polymer chain. While some of the soil particles may be merely surrounded by polymer structure without actually being bonded chemically to the structure, for the most part, the soil particles enter into and become part of the chemical structure.

The nature of the chemical reaction described above, and the properties of the resulting soil product place a number of requirements on the monomer that is used in the present treatment.

Since the initial step in the present process is the linking of the monomer with the soil particles through a base exchange reaction, surface attraction, or other mechanism, depending on the particular soil composition, it is essential that the monomer be an ionizable, water-soluble salt. Since the organic part of the monomer is negatively charged, the cation part of the monomer must be polyvalent in order that a positively charged complex monomer ion (such as the



ion described above) will be available for base exchange with the negatively charged or surface attracted soil particles. A polyvalent cation is further required if this cation is to serve as a link in cross-polymerization.

It is evident from the very purpose of the present soil treatment that the monomer must be capable of forming a polymer which is insoluble in water, and further that the monomer be capable of polymerization under normal outdoor temperature and pressure conditions. Finally, in order to produce a soil product of the requisite strength it is necessary that the monomer be capable of forming a cross-linking polymer, either of itself, or by the addition of a chemical which aids in cross linking.

We have found that certain of the acrylates and substituted acrylates satisfactorily meet all of the above requirements, as for example, strontium acrylate, zinc acrylate, and calcium methacrylate. Calcium acrylate has been found to be especially suitable for use as a monomer in the present soil treatment.

As has already been indicated, the use of the present soil treatment in the solidification of natural soils in situ requires a polymerization process that may be carried out at normal outdoor temperatures and without appreciable molding pressure.

The polymerization of a soil treated with calcium acrylate or other suitable monomer is effected according to the present invention with the aid of suitable reduction-oxidation catalysts. Such catalysts are generally termed "redox" catalysts, and the term will be so employed herein.

In the redox catalyst system the activator, a reducing agent, reacts with the catalyst, an oxidizing agent, to produce free radicals, which initiate the polymerization of the monomer according to well-known principles.

The particular redox system that is most effective and the amount used in the present soil treatment will depend on the constituents of the soil, the treating monomer used, the ambient temperature, and the time desired for the initiation of the polymerization reaction. It is essential that neither the oxidizing catalyst nor the reducing activator form an insoluble precipitate with the cation of the monomer since that would prevent a large amount of the catalyst or activator from entering into the reaction. It is desirable, although not essential, that neither the cation of the oxidizing catalyst nor the cation of the reduction activator form an insoluble precipitate with the monomer anion, since that would remove a certain portion of the monomer from solution and render it ineffective. According to the procedure outlined above, it is essential that the redox catalyst system not form precipitates with calcium, and desirable that the redox catalyst system not form precipitates with the acrylate anion.

A number of redox catalysts have been found effective to promote satisfactory polymerization for in situ treatment. Thus, we have found that the persulfates are effective as oxidizing agents, while the thiosulfates work well as reducing agents to provide satisfactory polymerization of the soil-monomer system in the present invention. An ammonium persulfate-sodium thiosulfate system has been found to be particularly effective for the purposes of the present invention.

Certain peroxides have likewise been found to be effective as oxidizing agents when used in conjunction with appropriate reducing agents. By way of example, tertiary butyl hydroperoxide and sodium thiosulfate make a particularly effective redox system for use in the present invention. Other reducing agents such as hydroxylamine hydrochloride, hydrazine hydrate, and tetramethylene pentamine have also been found effective in conjunction with the appropriate oxidizing agents in the present invention.

The choice of an appropriate redox system is influenced by the desired gel time of the soil treatment reaction. The gel time is the interval between the addition of the redox catalyst system and the commencement of polymerization. If this gel time is of the order of a minute or less for a particular system, the solidification may be initiated before the soil system has been properly prepared. For example, if the redox catalyst chemicals are added to a soil system along with the calcium acrylate, it is preferable that the gel time be long enough to allow thorough mixing of the treatment materials with the soil before polymerization takes place. In the case of a surface soil treatment it may be further desirable to allow sufficient time to permit smoothing the soil surface and compaction before the polymerization takes place. The amount of time needed for the mechanical op-

erations of mixing, smoothing, and compaction, depends largely on the type of soil system that is being treated and the nature of the mechanical equipment available to perform the mixing, smoothing, and compaction.

By appropriate selection of catalyst concentration, the gel time may be varied so that polymerization commences within one minute or less, or may be delayed up to several hours. For example, using an ammonium persulfate-sodium thiosulfate catalyst system on a sandy clay soil treated with calcium acrylate, a 5% concentration of catalyst (based on the weight of the acrylate present in the soil) will provide a gel time on the order of 80 minutes, while a 50% concentration of catalyst, under similar conditions, will result in a gel time on the order of one minute, and the use of 20 to 25% catalyst will provide a gel time of about 6 to 8 minutes.

While the amount of catalysts used has a marked effect on gel time, the catalyst concentration does not affect significantly the strength of the treated soil, so long as sufficient catalyst is employed to effect polymerization. Neither does it appear that the relative amounts of the two constituents of the redox system are critical, and in general approximately equal proportions of the two chemicals will be found satisfactory.

The soil water content or the amount of water present in the soil has a considerable influence on the chemical reaction that takes place, the mode of application of the treating materials, and the properties of the soil product resulting from the treatment. It is one of the features of the present invention that it is possible to treat effectively soils of various water contents. The term water content, as used here, refers to the ratio of weight of water present in a given soil sample to the weight of "dry soil" in the sample, obtained by drying under prescribed conditions.

The present treatment may be used to stabilize soils at a water content less than or greater than the liquid limit of the soil. It is not primarily a waterproofing treatment intended to protect an originally dry soil from increases in water content, but rather considers the soil water as part of the soil system to be stabilized.

A certain amount of free soil water is essential to the present treatment, in order that some of the chemicals added to the soil can go into solution, be ionized, and enter into the base exchange reaction with the soil. Most natural soils have enough water in them to meet the necessary requirement for polymerization, even though a considerably greater amount of water might be required if all of the monomer that is used in the treatment had to be dissolved. It is not necessary, however, that all the monomer be dissolved, as it appears that such portion of the monomer as does not dissolve and base exchange with the soil particles is nevertheless available for polymerization in the final phase of the treatment. In some instances, increasing the water content of a soil may be desirable to aid in obtaining satisfactory mixing of the soil and chemicals in carrying out the treatment.

The addition of the monomer to the soil and the polymerization of the soil-water-monomer system has two important effects on the behavior of the soil in respect to water. In the first place, the formation of an insoluble polymer in which the soil particles become part of the polymer is effective to decrease the permeability of the soil, due to the formation of a continuous soil-poly-

mer-water structure. In this sense, the present treatment acts as a waterproofing agent on the soil. The second effect is that the water contained in the soil before treatment is stabilized in the soil-polymer structure. In other words, the soil water is more closely held to the soil structure by the formation of the polymer structure. The effect of this is to retard changes in the water content of the soil. The soil will retain its water longer in a dry atmosphere and absorb surface water more slowly than an untreated soil system.

By stabilizing the water content of a soil, the present treatment renders a soil structure less subject to changes in volume due to changes in water content. It is well known that a soil decreases its volume considerably when its water content decreases and this may cause serious cracking of a soil surface. Since treated soil is less subject to changes in water content, it follows that it is also less subject to cracking due to shrinkage. It has been found that the total amount of shrinkage, as well as the rate of shrinkage, is less in a soil that has been treated according to the procedures of the present invention.

In carrying out the treatment the monomer and catalysts are incorporated in the soil in a manner to insure thorough mixing. In the case of a roadway, runway or the like, the soil to be treated may be taken up, mixed with chemicals and then returned to the ground, leveled, and compacted by rolling equipment if desired. Alternatively, the chemicals may be incorporated directly in the soil by distributing and mixing on the subgrade by mechanical apparatus employing rotating tines or teeth. For sub-surface treatments, such as dam cores, the treating chemicals may be injected as a solution or slurry into the soil from pipes driven into the ground.

The mechanical equipment and the mode of introducing the chemicals into the soil must be such that chemicals and soil have been mixed before polymerization begins to take place in order that the mixing equipment not be immobilized by the solidifying soil. The monomer and the catalysts may be added as a single mixed powder provided the gel time of the soil-monomer mixture is sufficiently long so that the mechanical equipment is able to complete the mixing of the soil and chemicals before the polymerization begins to take place. The catalysts may be added separately after the monomer has been thoroughly mixed with the soil if the gel time is too short to allow a simultaneous addition of the treating chemicals.

It may be further desirable, depending on the type of mechanical equipment used, that the treated soil be reapplied, smoothed, and possibly compacted before polymerization begins to take place. Alternatively, the soil may be taken up and mixed with the treating chemicals in an amount to provide a relatively short gel time and reapplied to the surface by extruding the soil-monomer mixture in the form of a sheet while it is in the process of polymerizing.

The manner in which the treatment operates to provide a roadway or the like without the provision of a foundation is illustrated in Fig. 5. The layer of treated soil has, as a result of the treatment, sufficient flexibility and tensile strength to function as a membrane to spread the load over a substantial area of the subgrade. In this way relatively thin layers of treated soil, for example from 1½ to 3 inches in depth, are

effective to support vehicular traffic even over relatively weak subgrades. The technique is in marked contrast to more conventional procedures which require a firm foundation beneath the surface, whether the surface be rigid, as provided by cement, or shear-resistant, such as given by bitumen treatment.

The amount of monomer used depends on the character of the soil and the type of product desired. Increasing the amount of acrylate causes an increase in tensile strength and flexibility. Amounts of acrylate ranging from 4% to 25% of dry soil weight have been used successfully. Below about 4% it is difficult to secure proper distribution. From 5% to 10% of acrylate has been found satisfactory from the standpoint of load carrying ability for vehicular traffic, although greater amounts may be used where cost considerations permit.

The calcium acrylate treatment can increase the tensile strength of a soil from zero to very substantial values. For example, representative results obtained by using approximately 10% acrylate and suitable amounts of catalysts (2% to 20%, depending on gel time desired) on sandy clay soils at 35% to 50% water content show tensile strengths up to 50 lbs. per square inch. With less mixing water, greatly increased compressive strengths are obtainable for applications where such characteristics are desired. Thus, at 16% water content, a 10% acrylate treatment has shown an increase of compressive strength from an initial 40 lbs. per square inch to approximately 600 lbs. per square inch.

The present soil treatment may be improved in certain instances by the addition of chemicals which form copolymers in the soil structure. Acrylonitrile and ethylene glycol diacrylate, for example, have been used to effect copolymerization with calcium acrylate to improve the tensile strength of the product.

The treatment of the present invention has been found effective on soils of widely different characteristics. Appropriate variations in mixing water content may of course be required in certain cases, depending on the fineness of the particles. Also, the mixing technique may have to be suited to the special requirements of the soil. Nevertheless, over a wide variety of conditions the treatment is operative to form a flexible product of significant tensile strength with marked ability to withstand the effects of water.

What is claimed is:

1. A method of forming a stabilized structure composed essentially of natural soil and a stabilizer therefor, which consists essentially of admixing with the natural soil a monomeric water soluble acrylate of a polyvalent metal, and a reduction-oxidation catalyst, forming the mixture into the desired structural form, and thereafter polymerizing the monomeric acrylate in the presence of sufficient moisture to at least partially ionize said acrylate and said catalyst, the polymerization being carried out at atmospheric temperature and pressure, to produce a stable soil-polymer-water structure in said desired form.

2. The process of claim 1 in which the soil is formed into a stabilized structure in situ.

3. The process of claim 1 in which the monomeric water soluble acrylate of a polyvalent metal is utilized in an amount exceeding about 4% of the dry weight of the soil.

4. The process of claim 1 wherein the water soluble acrylate of a polyvalent metal is used

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in an amount equal to from about 4% to about 25% of the dry weight of the soil.

5. The process of claim 1 in which the water soluble acrylate of a polyvalent metal is calcium acrylate.

6. The process of claim 1 in which the water soluble acrylate of a polyvalent metal is zinc acrylate.

7. The process of claim 1 in which the reduction-oxidation catalyst consists essentially of a mixture of ammonium persulfate and sodium thiosulfate.

8. The process of claim 1 in which the reduction-oxidation catalyst consists essentially of a mixture of tertiary butyl hydroperoxide and sodium thiosulfate.

9. The process of claim 1 in which the reduction-oxidation catalyst is present in an amount equal to from about 5% to about 50% of the weight of the water soluble acrylate of a polyvalent metal which is utilized.

10. The method of claim 1 in which there is utilized in conjunction with the water soluble acrylate of the polyvalent metal, a monomer different from said acrylate which is capable of copolymerizing therewith under the conditions.

11. A method for forming a stabilized structure composed essentially of natural soil and a stabilizer therefor, which consists essentially of mixing the natural soil with a monomeric water soluble acrylate of a polyvalent metal, forming the mixture into the desired structural form, base-exchanging said monomeric acrylate with said soil, and thereafter polymerizing said monomeric acrylate in the presence of a reduction-oxidation catalyst and sufficient moisture to at least partially ionize said acrylate and said catalyst, the polymerization being effected at atmospheric temperature and pressure, to produce a stable soil-polymer-water structure in said desired form.

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12. The process of claim 11 in which the soil is formed into a stabilized structure in situ.

13. The process of claim 11 in which the monomeric water soluble acrylate of a polyvalent metal is utilized in an amount exceeding about 4% of the dry weight of the soil.

14. The process of claim 11 wherein the water soluble acrylate of a polyvalent metal is used in an amount equal to from about 4% to about 25% of the dry weight of the soil.

15. The process of claim 11 in which the water soluble acrylate of a polyvalent metal is calcium acrylate.

16. The process of claim 11 in which the reduction-oxidation catalyst consists essentially of a mixture of ammonium persulfate and sodium thiosulfate.

17. The process of claim 11 in which the reduction-oxidation catalyst consists essentially of a mixture of tertiary butyl hydroperoxide and sodium thiosulfate.

18. The process of claim 11 in which the water soluble acrylate of a polyvalent metal is calcium acrylate and in which the reduction-oxidation catalyst consists essentially of a mixture of ammonium persulfate and sodium thiosulfate.

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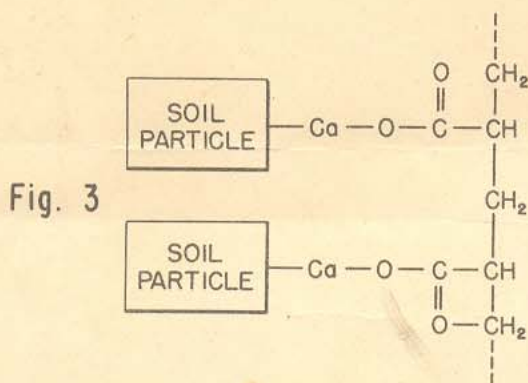
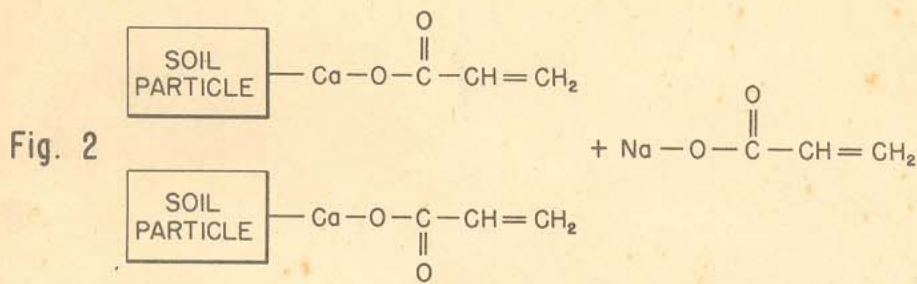
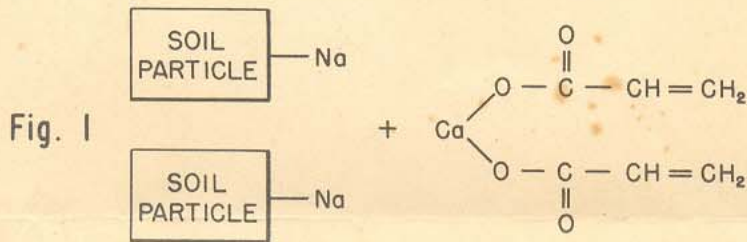
Sept. 8, 1953

V. F. B. DE MELLO ET AL  
STABILIZATION OF SOILS

2,651,619

Filed Jan. 25, 1951

2 Sheets-Sheet 1



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