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SOIL STABILIZATION

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This invention relates to soil stabilization and more 15 particularly, to a method of solidifying soil so that it will remain cohered under conditions of high strain.

For many years great difficulty has been experienced in the construction of roadways and airfields on certain types of soil, such as the various clays, which form very fluid, gummy muds and are therefore incapable of supporting heavy weight. Similarly, sand is unsuitable for the support of heavy vehicles in many instances. In order to overcome these difficulties, portable steel mats have been used, and of course, concrete roadways and airport runways have been extensively employed. These have the disadvantage that they require the transportation of large quantities of heavy construction materials, sometimes at great distances and often where there are inadequate means for transportation.

It is an object of this invention to provide a means for stabilizing soils and sands to give them sufficient rigidity and strength to support heavy weights, i. e., motor vehicles, military equipment, aircraft, and the like.

It is another object of the present invention to prevent soil erosion.

A further object of the present invention is to increase markedly the viscosity of fluid muds.

Still another object of the present invention is to solidify soil.

It is still a further object of the present invention to impart rubber-like properties to soils.

These and other objects are attained by incorporating in the soil or sand to be stabilized a water-soluble or water-dispersible polymerizable composition containing an acrylamido derivative, which composition is capable of being converted to a water-insoluble state while in association with the soil or sand.

The following examples in which the proportions are 50 given in parts by weight are merely illustrative. It is not intended that the scope of the invention be limited to the details therein set forth.

Example 1

500 parts of montmorillonite clay 50 parts of methylol acrylamide 2 parts of ammonium persulfate 0.5 part of sodium thiosulfate 225 parts of water

A solution of the methylol acrylamide, the ammonium persulfate and the sodium thiosulfate in the water is made acid with sulfuric acid to a pH of about 4 and then mixed with the clay. The resulting mixture is spread on the ground from which the clay was taken in a layer of about 4-8 inches thick. After about 12 hours at temperatures of about 25 degrees C., a rigid hard surface is obtained.

Example 2

500 parts of kaolinite 50 parts of methylol acrylamide 2

50 parts of acrylamide 2 parts of ammonium persulfate 0.5 part of sodium bisulfite 300 parts of water

A solution of the methylol acrylamide, acrylamide, ammonium persulfate and sodium bisulfite in the water is acidified to a pH of about 3.5 with sulfuric acid and then mixed with the clay. A layer of the mixture about 4-10 inches thick is spread on the soil surface from which the kaolinite was taken and after about 12 hours at about 25 degrees C., a hard, rigid surface is obtained. In thick sections very heavy vehicles may be readily supported.

Example 3

1000 parts of montmorillonite clay
25 parts of acrylamide
25 parts of methylol acrylamide
25 parts of partially polymerized methylolacrylamide
25 parts of calcium acrylate
5 parts of ammonium persulfate
1 part of sodium bisulfite
600 parts of water

The partially polymerized methylolacrylamide is prepared by polymerizing methylolacrylamide in aqueous
solution in the presence of about 1% of ammonium persulfate at a temperature of about 60 degrees C. until a
viscous solution or dispersion results. Incorporation of
this partially polymerized methylolacrylamide, the acrylamide, the methylolacrylamide, the calcium acrylate, the
ammonium persulfate and the sodium bisufite with the
water results in the formation of a solution or dispersion
which is made alkaline with sodium hydroxide to a pH
of about 11. This aqueous material is mixed with the
clay and the mixture then spread on the surface from
which the clay was taken and allowed to polymerize for
12-24 hours at a temperature of about 20 degrees C.
A tough, flexible surface results.

Example 4

500 parts of sand 100 parts of methylolacrylamide 2 parts of ammonium persulfate 0.5 part of sodium bisulfite 240 parts of water

A solution of the methylolacrylamide, ammonium persulfate and sodium bisulfite in the water is made acid with sulfuric acid to a pH of about 3.5-4. This is now mixed with the sand and the mixture spread in a layer about 6 inches thick on the sub-sand surface from which the sand used was removed. Polymerization is allowed to take place for about 12-24 hours at a temperature of about 25 degrees C. A hard, strong surface is obtained which is quite capable of supporting heavy loads.

Any polymerizable composition containing an acrylamido derivative, which composition is water-soluble or water-dispersible in the concentration used and is at the same time capable of being converted to a water-insoluble state by polymerization processes, either of the condensation or vinyl type or of a combination of the two, may be used in our process to produce our new stabilized soil compositions.

The invention contemplates primarily the addition to soil of a water-soluble or water-dispersible methylol acrylamido derivative which is methylolacrylamide, a methylol-polyacrylamide or a poly(methylolacrylamide). These materials may be prepared in general in accordance with the teaching of U. S. Patent No. 2,173,005. A water-soluble poly(methylolacrylamide), for example, may be prepared as follows:

30.4 parts of isopropanol, 364 parts of demineralized

water and about 10 parts of 0.1 M sulfuric acid are placed in a suitable vessel equipped with temperature indicating means, an inert gas inlet, means for agitation and a reflux condenser, and heated to about 40 degrees C. 500 parts of a 20.2% aqueous solution of methylolacrylamide are added and the resulting solution, which has a pH of 4.7, is heated to 60 degrees C., at which point about 2 g. of potassium metabisulfite (K2S2O5) and 4 g. of ammonium persulfate [(NH4)2S2O8] dissolved in 100 parts of water are added. Polymerization is permitted to continue for 1 hour while maintaining the temperature between about 60 degrees-65 degrees C. The polymer solution is then cooled rapidly and adjusted to a pH of 8.5 with 26 parts of 10% aqueous sodium hydroxide.

Mixtures of these methylol acrylamido derivatives may also be used, cf. Example 3, as well as mixtures of one or more of them with no more than 50% of other watersoluble or water-dispersible acrylic compounds containing no methylol substitution such as acrylamide, N-alkylacrylamides wherein the alkyl group contains up to 4 carbon atoms such as N-t-butylacrylamide, methacrylamide, acrylonitrile, methacrylonitrile, acrylic acid, methacrylic acid, salts of either of these acids, i. e., calcium acrylate, alkyl esters of either of these acids, i. e., methyl methacrylate, hydroxyethyl acrylate, and the like, cf. Examples 2 and 3. Minor amounts i. e., less than 50%, of other monovinylidene compounds such as vinyl acetate, vinyl chloride, vinyl pyridine, styrene, substituted styrenes, for example, the mono- and di-chlorostyrenes, the aminostyrenes, o-, m- and p- methyl styrenes, alpha, para-dimethylstyrene, 2,4-dimethylstyrene, etc., monoallyl phthalate, methyl vinyl ketone, allyl amine, allyl alcohol, and the like may also be used in conjunction with the methylol acrylamido derivatives. In selecting any particular unmethylolated monovinylidene compound, or in determining the relative proportions of methylol acrylamido derivative and selected unmethylolated monovinylidene compound to be used, it must be borne in mind that the mixture should be water-soluble or water-dispersible so that it may be readily applied to the soil to be stabilized.

While we do not wish to be limited to any particular theory, we believe that soil or sand treated with polymerizable methylolacrylamido derivatives according to the process of the present invention is stabilized because 45 it contains polymeric material which is cross-linked by reason of having undergone two distinct types of polymerization, i. e., polymerization of the vinyl groups and condensation of the methylol groups, and is therefore water-insoluble. This theory is substantiated by the fact 50 that a soil-polyacrylamide mixture readily disintegrates in the presence of water because polyacrylamide, being essentially a linear polymer, is soluble in water. If acrylamide, however, or any other unmethylolated monoacrylamido derivative such as, for example, N-t-butyl- 55 down to neutrality, may be used. acrylamide, is copolymerized with a polymerizable monovinylidene compound of the type listed above as suitable for copolymerization with the methylol acrylamido derivatives, so selected that the polymerizable mixture is water-soluble or water-dispersible and the polymerized 60 product is water-insoluble, such copolymerizable compositions are useful in our process. Thus, for example, copolymers of acrylamide with calcium acrylate are particularly useful. Acrylamide may also be used by aftertreating soil containing polyacrylamide with formalde- 65 hyde whereby the soil-resin mixture becomes not disintegrable by water.

The present invention is intended to cover only suitable polymers and copolymers of the methylol acrylamido derivatives, and copolymers with monovinylidene com- 70 pounds of acrylamido derivatives either methylolated or The use for soil stabilization of certain copolymers of acrylic acid derivatives, including the acrylamido and methylolacrylamido derivatives, with polyvinyl com4

plication of one of the present inventors, Russell L. Morgan, with John J. Padbury, Serial No. 236,454, filed July 12, 1951, entitled "Soil Stabilization," now abandoned.

Polymerization of the vinyl groups of the compounds used in accordance with our invention is effected preferably with any of the usual water-soluble oxygen-containing catalysts, such as the ammonium, potassium and sodium persulfates, hydrogen peroxide, the alkali metal and ammonium chlorates and the like. It is generally desirable to use a redox catalyst system of an oxygencontaining compound with a reducing agent, such as sodium thiosulfate, sodium or potassium bisulfite, etc., a typical combination being the chloric acid-bisulfite system described in the copending application of Arthur Cresswell, Serial No. 208,797, filed February 1, 1951, now abandoned. We are not limited to any particular quantity of catalyst but in general from about 0.1% to about 10%, based on the weight of polymerizable monomers may be used.

In order that the methylol groups of the compounds used be polymerized in relatively short periods of time, it is desirable that the solutions be either strongly alkaline or strongly acidic. Certain redox systems (e. g. chloric 25 acid-bisulfite) require acid conditions, and others operate but under acid conditions. Hence, polymerization below pH 7 is preferred. If acid polymerization is contemplated, any desired acidic material including sulfuric acid, hydrochloric acid, phosphoric acid, diammonium hydrogen phosphate, ammonium chloride, ammonium sulfate, etc., may be used for this purpose. cases, it may be desirable to use organic acids but since they are more expensive, this is generally not an economical procedure. However, acetic acid, oxalic acid, tartaric 35 acid, phthalic anhydride and other acids may be used.

While the quantities of acid employed may be varied widely from very small amounts, which will merely produce an acid reaction, it is generally preferable that the pH be relatively low and of the order of 3.5-4.

In some cases, particularly with soils containing acidadsorbing or reacting materials, it may be more desirable to polymerize the methylol groups under alkaline conditions. For such purposes any water-soluble alkali may be used, but in general, sodium carbonate, sodium hydroxide, ammonium hydroxide, potassium hydroxide and calcium hydroxide are preferred because they are relatively inexpensive as compared to other alkaline materials. Organic bases such as guanidine carbonate, however, may be used.

When alkaline materials are used to catalyze the polymerization of the methylol groups, it is preferable that the pH be relatively high, of the order of about 11, but if it is not necessary to polymerize the methylol groups rapidly, lower degrees of alkalinity, ranging all the way

In the case of alkaline soils it is possible to use a catalyst system comprising an amine or the activator for the vinyl polymerization. Examples of activators for peroxy type catalysts such as persulfates are polyamines, i. e., diethylene triamine tetraethylene pentamine, etc., triethanolamine, dimethylaminopropionitrile, dimethylaminoacetonitrile, etc.

The gel formation of a particular resin may vary depending upon whether polymerization is effected in the presence of acid or alkali, and this factor should also be considered in determining the polymerization conditions. If, for example, the methylol groups of methylolacrylamide are made to condense under alkaline conditions, a more flexible, tougher gel is obtained than when condensation takes place in the presence of acid. Under at least some circumstances, therefore, alkaline condensation of methylolacrylamide is to be preferred.

Our invention is applicable to all types of clays and sands and various soils containing mixtures of such mapounds is described and claimed in the copending ap- 75 terials which are normally soft or muddy, and which

The ratio of polymerizable material to soil may be varied widely, but generally should be within the range of about 3-15 parts by weight of soil to 1 part by weight of polymerizable material. Ordinarily, the polymerizable material is dissolved or dispersed in water to form a solution or dispersion which is mixed with the soil. The concentration of the solution or dispersion and the quantity used should be regulated so that the concentration of water in the final mixture of soil and stabilizing additive is between about 40% and 70% by weight, and preferably about 50% or 60%. The proportion of water used determines to some extent the properties of the resulting stabilized soil.

The polymerizable material may be incorporated with the soil in any desired manner as, for example, by mixing in a revolving drum. Another method of application which may sometimes be employed is spraying an aqueous solution or dispersion of the polymerizable material onto the ground which it is desired to toughen. This expedient may not result in sufficient penetration for some purposes, however, although the difficulty can often be at least partially overcome by plowing the soil either before or after spraying or simultaneously therewith. This can conveniently be done with the "roto tiller" type of plow having revolving tynes which thoroughly mix the top few inches of soil.

In order to ensure sufficient strengthening of any given section of ground for the support of heavy weight, a surface of from about 4–12 inches of soil treated according to the process of the present invention should be provided. The actual depth necessary will, of course, vary depending upon how fluid the soil is to begin with or, in other words, how much solidifying is required.

As used in the present specification and claims the term "stabilize" as applied to soil means to impart to the soil high viscosity, solid or rubber-like properties. Moreover, the expression "water-soluble" as used is intended to be inclusive of the expression "water-dispersible."

We claim:

- 1. A process for treating soil which comprises incorporating a polymerizable water-dispersible material substantially free of alkylidene bisacrylamides and of the group consisting of methylol acrylamide, methylol polyacrylamide and polymethylol acrylamide into soil and polymerizing the polymerizable matter in the resulting composition in the presence of an oxygen-containing polymerization catalyst at naturally occurring temperatures to a substantially water-insoluble state in contact with natural soil substantially within the surface of the earth in the presence of water.
- 2. A process according to claim 1 in which said material is polymethylol acrylamide.
- 3. A process according to claim 1 in which said material derivative is admixed with a water-dispersible copolymerizable vinylidene monomer.
- 4. A process according to claim 1 in which said material derivative is methylol acrylamide and is admixed with a compound of the group consisting of acrylic acid, methacrylic acid and salts of said acids.
- 5. A process according to claim 1 in which 1 part by weight of polymerizable material is incorporated into at least 3 parts by weight of soil.

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- 6. A process for treating soil which comprises incorporating 1 part by weight of a polymerizable water dispersible material substantially free of alkylidene bisacrylamides and containing a major proportion of an acrylamide and containing a major proportion of an acrylamide, methylol polyacrylamide, and polymethylol acrylamide and a minor proportion of a compound of the group consisting of acrylic acid, methacrylic acid and salts of said acids into at least 3 parts by weight of soil and polymerizing the polymerizable matter in the resulting composition at naturally occurring temperatures to a substantially water-insoluble state in contact with natural soil substantially within the surface of the earth in the presence of an aqueous solution of an oxygen-containing polymerization catalyst.
 - 7. A process according to claim 6 in which said compound is calcium acrylate.
 - 8. A process according to claim 6 in which said acrylamido derivative is methylol acrylamide.
 - 9. A process according to claim 6 in which said acrylamido derivative is methylol acrylamide and said compound is calcium acrylate.
 - 10. A process according to claim 6 in which a quantity of soil is removed from the ground, mixed with water along with said catalyst and said polymerizable material, the resulting mixture deposited in the same approximate ground location from which the soil was removed and the mixture polymerized in situ.
- 11. An earthen mass which comprises a soil-polymer 30 composition prepared according to the process of claim 1.
 - 12. An earthen mass which comprises a soil-polymer composition prepared according to the process of claim 6.
 - 13. An earthen mass which comprises a soil-polymer composition prepared according to the process of claim 9.
 - 14. A process according to claim 1 in which said material is methylol polyacrylamide.
 - 15. A process according to claim 1 in which said material is methylol acrylamide.
- 16. A process for treating soil which comprises incorporating a polymerizable water-dispersible material
 substantially free of alkylidene bisacrylamides and of the
 group consisting of methylol acrylamide, methylol polyacrylamide and polymethylol acrylamide into soil and
 converting the resulting composition to a substantially
 water-insoluble state in contact with natural soil substantially within the surface of the earth in the presence of
 water, an oxygen-containing polymerization catalyst and
 polymerizing the polymerizable matter in said composition without the application of artificial heat.

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