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3,208,226

PROCESS FOR STABILIZING SOIL

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No Drawing. Filed Jan. 10, 1963, Ser. No. 250,496
8 Claims. (Cl. 61—36)

This application is a continuation-in-part of my earlier application Serial No. 140,254 filed September 25, 1961, entitled, Process for Stabilizing Soil, now abandoned.

This invention relates to a process for stabilizing water-permeable soil in order to render the same substantially water-impermeable comprising applying an aqueous dispersion of an acid-catalyzed thermosetting urea-formaldehyde resin to the soil and curing said resin at ambient temperatures to substantially water-insoluble thermosetting state. Still further this invention relates to the soil stabilized by the process of the present invention.

One of the objects of the present invention is to stabilize water-permeable soil to a substantially water-impermeable state. A further object of this invention is the grouting of water-permeable soil so as to render the same substantially water-impermeable. A further object of the present invention is to convert water-permeable soil to substantially water-impermeable soil. These and other objects of the present invention will be discussed in greater detail hereinbelow.

With the development of commerce it has been found necessary on many occasions to alter the physical characteristics of soil in order to increase the unconfined compressive strength of said soil or to alter its water permeability characteristics. In the construction of roadways, airfields, runways, railroad beds and the like, it has frequently been found that when a sandy soil is physically present as the upper and/or lower strata where such roadway is to be established, that the soil lacks the necessary unconfined compressive strength so as to be able to tolerate great weights as are to be found in automobiles, trucks, airplanes, locomotives and railroad cars. In the past when such soil conditions were discovered, it became necessary in absence of a solution to the problem to detour around such sandy area at considerable expense or to reinforce the soil by superimposing thereon large quantities of a compactable gravel but again at considerable expense. Similarly in the drilling of oil wells and in mine shafts and tunnels it has frequently been found highly desirable to endeavor to seal off said well, shaft or tunnel in certain areas in order to prevent moisture penetration and seepage at subterranean levels frequently hundreds of feet below the earth's surface.

Additionally, in the construction of buildings where the water table would vary from just a few feet below the earth's surface to a level above the floor in a basement, water seepage and penetration problems have been experienced. In the latter instance, when these problems are anticipated in advance, suitable drainage fields can be set up at some expense which will divert the flow of water and thereby avoid basement flooding. However, in certain instances, this flooding is not detected until after the foundation has been completely installed and thereafter the drainage fields can be installed only with great difficulty and expense. The process of the present invention is applicable also to these oil wells, subterranean shafts and basement foundations wherein a suitable hole is drilled in the desired location and to the required depth and an aqueous dispersion of the acid-catalyzed urea-formaldehyde resin can be pumped down the drilled hole to the area required and upon curing the resinous material at the temperature of its surrounding, i.e., the ambient temperature, soil that previously displayed a water-permeabil-

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ity characteristic is converted to one having substantially water-impermeability.

The types of soils to which the present invention is applicable are almost without number so long as they possess initially the characteristics of water-permeability and substantially low unconfined compressive strengths. More specifically, the process of the invention is applicable to fine clays or very coarse sands depending upon the average particle size of the soil material being grouted and/or stabilized. The particle size of the soil to be treated will on the average vary between about 0.074 mm. and 2 mm. wherein the effective diameter of 90% of the particles in the soil sample falls within the stated range. The effective diameter of a soil particle is the largest diameter of a particle of varying diameter. The depth to which the soil is treated in accordance with the concept of the present invention may be varied very widely depending upon the requirements of the soil after treatment. As a consequence the depth of treatment can vary from a few feet to 10, 20 or 50 feet below the earth's surface, in the instance of roadways for automobiles, air fields or railroads, or the treated area may be completely subterranean, i.e., beginning at a point significantly below the surface of the earth and extending downwardly to whatever depth is required as in oil wells, mine shafts and tunnels.

The urea-formaldehyde resins used in the process of the present invention are standard articles of commerce that are available from a plurality of commercial sources. These resins are prepared by reacting urea and formaldehyde in mol ratios between 1:1 and 1:4 respectively. Preferably one would use between about 1:1.5 and 1:2.5 mols urea to formaldehyde respectively. Generally for optimum results the mol ratio is about 1:2 urea to formaldehyde respectively. The urea and the aqueous solution of formaldehyde are reacted with one another to produce a resin syrup that is in a thermosetting state but capable of being converted to a thermoset state. Although these resins are available and may be used in a syrup form, they are sometimes available in a spray dried form which needs to be redispersed in water to the desired solids content. For the purposes of the present invention the solids content of the resin may be varied from about 20% to about 40% by weight of resin solids based on the total weight of the aqueous resin dispersion. Preferably one would use between about 25% and 35% resin solids solutions or dispersions. The viscosity of these resin dispersions in water may be varied from about 5 centipoises up to about 50 centipoises and for the most part are varied directly within this range with the solids content.

The catalytic material used to convert the urea resin to a thermoset state at ambient temperature is an acidic material which has a dissociation constant varying between about 10^0 to 10^{-5} . The amount of acidic material used in the practice of the process of the present invention will depend in significant measure upon the acidic strength of the catalytic material as well as the conditions of cure external of the resin composition such as the temperature of the soil and the pH characteristic of the soil as well as the amount of time required to convert the resin to a thermoset state. If the soil is already acidic, one need not take into consideration any variation or effect on the acid-catalyzed resin dispersion by the soil but if the soil is neutral or slightly alkaline one would need to increase the amount of acidic material present in order to compensate for such neutrality or alkalinity. Still further if the soil to be treated is at or below the earth's crust during summer time conditions when the soil is exceedingly warm such as 80° F.—120° F. the heating effect of the soil will reduce the need for larger quantities of acid catalysts in order to accomplish the cure of the resins within the same period of time required to cure a comparable resin dispersion applied to a soil during the

fall or spring seasons when the temperature of the soil may be 35–60° F. For subterranean application it may well be worthwhile to make a soil temperature determination before the application of the resinous material thereto in order to determine how much or how little acid catalyst is required in order to accomplish the conversion to the thermoset state within a determined period of time. Among the materials which may be used in the practice of the process of the present invention are the organic and inorganic acids and their respective acidic salts. More particularly one may use such acidic materials as hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, acetic acid, chloroacetic acid, trichloroacetic acid, ammonium bisulfate, sodium bisulfate, ammonium chloride, ammonium nitrate, oxalic acid, maleic acid, paratoluene sulfonic acid, aniline hydrochloride and the like. The amount of the acidic catalytic material used in the practice of the process of the present invention may be varied between about 0.3% and 17% by weight based on the weight of resin solids in the dispersion. When the lower catalyst concentrations are used one will experience a longer gel time, i.e., a longer period of time before the development of a gel in the resinous composition. When the gel point is reached cure continues until a substantially completely thermoset condition is achieved and frequently the longer the gel time the lower strength development is experienced in the stabilized soil.

In order to prepare soil samples for testing purposes in order to insure that the tests were carried out under practical operating conditions the soil to be treated was prepared in the following manner. Several samples of the soil were washed and dried. All of the soil not passing through a number 10 U.S. standard sieve mesh (2.0 mm.) was rejected. The remaining soil was riffled until a quantity of soil sufficient for the tests was obtained. This quantity was successively riffled until 32 samples were obtained containing about 500 parts by weight each. During the riffing procedure, only those separations which yielded charges differing in weight by less than 1% of the total charge being riffled were accepted. Failure to meet this specification required that the divided charge be recombined and again riffled until the differences in weight were within the specified amount. At this point, the weights of the charges were made equal by transfer of a small quantity from one sample to another on a pan balance. A screen analysis of one of these prepared charges was then made as representative of all of the charges. This analysis is shown in Table I set forth hereinbelow.

TABLE I.—PARTICLE SIZE DISTRIBUTION OF SOIL USED

Mesh Size	Screen Opening (mm.)	Cumulative Wt. Percent Finer Than—
10	2.00	100.00
30	0.59	77.57
40	0.42	56.61
70	0.21	16.62
100	0.149	8.70
140	0.105	4.43
200	0.074	2.20
325	0.044	0.34

The general procedure for the treatment of the soil which was followed in the subsequent examples required that a charge of the soil described hereinabove was placed in a Pyrex glass tubing measuring 38 mm. inside diameter. This tubing was fitted at the bottom with a fritted glass filter. The soil was wetted and compacted by passing water through from the bottom of the tube and the excess water allowed to drain off. The resin solution containing the stated percentages of the catalyst was poured on the soil mass in the glass tube and a nitrogen pressure amounting to 1 p.s.i. applied to give a constant head pressure. The resin solutions contained a trace amount of a water dispersible dye in order that the depth of penetra-

tion of the resin could be measured using an ultraviolet light to observe the depth of penetration of the dye after the resin was found to have gelled. This depth coincided with the depth measured from the length of the stabilized soil mass in samples which were firmly stabilized. Within one hour after gelling the stabilized soil mass was removed from the tube and immersed in water. Each soil sample was removed from the water bath 24 hours after gelation and the unconfined compressive strength of the cylinder was measured. The cylinders were previously cut to a maximum height of 4 inches. Strength tests were carried out on a Baldwin Tester at a crosshead speed of 0.05 in./min., measuring the maximum compressive strengths.

In order that the concept of the present invention may be more completely understood, the following examples are set forth in which all parts are parts by weight unless otherwise indicated. These examples are set forth primarily for the purpose of illustration and any specific enumeration of detail contained therein should not be interpreted as a limitation on the case except as is indicated in the appended claims.

Example 1

Eleven samples of sand of the particle size described hereinabove were treated with 11 different samples of urea-formaldehyde resin each catalyzed with 10% by weight based on the resin solids of sodium acid sulfate. These urea resin samples were substantially identical with one another except for their solids content and their initial viscosities in centipoises. The results of the above penetration tests and strength of the soil masses are listed in Table II hereinbelow together with the solids content of the resins and the initial viscosity of the resins used.

TABLE II.—VISCOSITY, DEPTH OF PENETRATION AND UNCONFINED COMPRESSIVE STRENGTHS FOR VARYING CONCENTRATIONS OF U/F RESINS

Ex.	Percent Solids for Resin Grout	Initial Viscosity of Grout (cps.)	Depth of Penetration (in.)	Unconfined Compressive Strength (p.s.i.)
1	15	4.9	5 $\frac{3}{4}$	(¹)
2	20	6.3	5 $\frac{3}{8}$	46.7
3	25	8.5	4 $\frac{3}{4}$	59.0
4	30	9.5	3 $\frac{1}{2}$	164.0
5	35	15.0	2 $\frac{1}{2}$	267
6	40	30.6	1 $\frac{1}{2}$	690
7	45	62.5	1 $\frac{1}{2}$	640
8	30	16.8	1 $\frac{3}{4}$	305
9	15	8.4	4 $\frac{3}{4}$	(¹)
10	30	3.7	10 $\frac{1}{4}$	(¹)
11	42	8.2	6 $\frac{1}{2}$	(¹)

¹ Insufficient cohesive strength to bind soil together.

Example 12

A sample of Ottawa sand (–20 +40 mesh rounded silica grains) is treated with an aqueous dispersion of a urea-formaldehyde resin having a mol ratio of 1:2 respectively in 28.3% solids solution, having a viscosity of 30 cps., catalyzed with 8.8% by weight, based on resin solids of concentrated hydrochloric acid (commercially available 36.8% aqueous solution) at 32° F. The gel point was reached in about 6 minutes.

Example 13

Example 12 is repeated in substantially all details except with a resin having a viscosity of 15 cps. at a temperature of 50° F. and the gel time is about 3 minutes.

Example 14

Example 12 is repeated in substantially all details except that the soil temperature is 70° F. and the resin viscosity is 7 cps. The gel time is slightly over 1 minute.

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Example 15

Example 12 is repeated in substantially all details except that the concentration of catalyst is increased to 17.4%. The gel time is about 3½ minutes.

Example 16

Example 15 is repeated in substantially all details except that the soil temperature is about 40° F. and the resin viscosity is 23 cps. The gel time is slightly over 2 minutes.

Example 17

Example 15 is repeated in substantially all details except that the soil temperature is 50° F. and the resin viscosity is 15 cps. The gel time is about 1½ minutes.

Example 18

Example 15 is repeated in substantially all details except that the soil temperature is 60° F., the gel time is about 1 minute and the initial resin viscosity is 13 cps.

Example 19

Example 15 is repeated in substantially all details except that the soil temperature is 70° F., the gel time is approximately 40 seconds and the initial resin viscosity is 7 cps.

Example 20

Example 15 is repeated in substantially all details except that the soil temperature is 80° F., the gel time is about 28 seconds and the initial resin viscosity is 5 cps.

Example 21

Example 12 is repeated in substantially all details except that the acid catalyst concentration is 26.5%. The gel time is about 2 minutes.

Example 22

Example 21 is repeated in substantially all details except that the soil temperature is 40° F., the gel time is about 1¼ minutes and the initial resin viscosity is 23 cps.

Example 23

Example 21 is repeated in substantially all details except that the soil temperature is 50° F., the gel time is just under 1 minute and the initial resin viscosity is 15 cps.

Example 24

Example 21 is repeated in substantially all details except that the soil temperature is 60° F., the gel time is about 40 seconds and the initial resin viscosity is 13 cps.

Example 25

Example 21 is repeated in substantially all details except that the soil temperature is about 70° F., the gel time is about 20 seconds and the initial resin viscosity is 7 cps.

Example 26

Example 21 is repeated in substantially all details except that the soil temperature is about 80° F., the gel time is about 15 seconds and the initial resin viscosity is 5 cps.

Example 27

Example 12 is repeated in substantially all details except that the acid concentration is 53%, the gel time is about 1 minute and the initial resin viscosity is 30 cps.

Example 28

Example 27 is repeated in substantially all details except that the soil temperature is 40° F., gel time is about 35 seconds and the initial resin viscosity is 23 cps.

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Example 29

Example 27 is repeated in substantially all details except that the soil temperature is 50° F., the gel time is about 30 seconds and the initial resin viscosity is 15 cps.

Example 30

Example 27 is repeated in substantially all details except that the soil temperature is about 60° F., the gel time is about 15 seconds and the initial resin viscosity is 13 cps.

Example 31

Example 27 is repeated in substantially all details except that the soil temperature is 70° F., the gel time is about 10 seconds and the initial resin viscosity is 7 cps.

Example 32

Example 27 is repeated in substantially all details except that the soil temperature is about 80° F., the gel time is about 6 minutes and the initial resin viscosity is 5 cps.

Example 33

A urea formaldehyde resin having a 28.3% solids solution in water is catalyzed with 17.6% of aniline hydrochloride and is applied to soil having a particle size of less than 2% +10 mesh and less than 1% -325 mesh at varying temperatures all other factors being held constant except as indicated hereinbelow.

TABLE III

Ex.	Temp., ° F.	Initial Viscosity, cps.	Gel Time (minutes)
33a-----	40	23	45
33b-----	50	15	28
33c-----	60	13	18
33d-----	70	7	9
33e-----	80	5	5

Example 34

Example 33 is repeated in substantially all details except that in the place of the aniline hydrochloride there is utilized the same weight of ammonium bisulfate. When applied to soil at varying temperatures and viscosities the following gel times are experienced.

TABLE IV

Ex.	Temp., ° F.	Initial Viscosity, cps.	Gel Time (minutes)
34a-----	32	30	7
34b-----	40	23	3½
34c-----	50	15	3
34d-----	60	13	2
34e-----	70	7	1¼
34f-----	80	5	1

Example 35

Example 34 is repeated in substantially all details except that the amount of ammonium bisulfate is reduced to 3.5%. At 70° F. a 7 cps. resin had a gel time of about 4½ minutes. When a portion of the catalyzed resin solution is injected into a sample of Ottawa sand (-20 +40 mesh, rounded silica grains) immediately after the catalyst addition, the gel time is the same as the gel time of the catalyzed neat resin. Furthermore this stabilized sand had an unconfined compressive strength of 45 p.s.i. about 30 minutes after the gelation point. A similarly treated sample after 76 minutes from gelation time had an unconfined compressive strength of 193 p.s.i. A further sample developed an ultimate strength of 280 p.s.i.

Example 36

A urea-formaldehyde resin solution containing 28.3% solids is catalyzed with 8.9% of concentrated sulfuric acid.

This resin is applied to a sandy soil having the same description as Example 33. The results are shown in Table V.

TABLE V

Ex.	Temp., ° F.	Initial Viscosity, cps.	Gel Time (seconds)
36a.....	68	8	70
36b.....	60	13	90
36c.....	50	15	140
36d.....	32	30	300

Example 37

Example 36 is repeated in substantially all details except that in the place of the sulfuric acid there is substituted the same amount of phosphoric acid. The gel time of an 8 cps. resin applied to the same kind of soil at 68° F. is 9½ minutes, whereas at 32° F. a 30 cps. resin applied to the same kind of soil has a gel time of about 30 minutes.

I claim:

1. A process for stabilizing water-permeable soil in order to render the same substantially water-impermeable comprising applying an aqueous dispersion of an acid-catalyzed thermosetting urea-formaldehyde resin having a solids content of between about 20% and 40% by weight based on the total weight of the dispersion and having an initial viscosity between about 5 centipoises and 50 centipoises and curing said resin at ambient temperatures to a substantially water-insoluble thermoset state, wherein said resin is catalyzed with an acidic material having a dissociation constant between about 10^0 and 10^{-5} and wherein the soil being treated has an average particle size sufficient to pass through a 10 mesh screen but retained substantially completely on a 200 mesh screen.

2. A process for stabilizing water-permeable soil in order to render the same substantially water-impermeable comprising applying an aqueous dispersion of an acid-catalyzed thermosetting urea-formaldehyde resin having a solids content of between about 25% and 35% by weight based on the total weight of the dispersion and having an initial viscosity between about 5 centipoises and 50 centipoises and curing said resin at ambient temperatures to a substantially water-insoluble thermoset state, wherein said resin is catalyzed with an acidic material having a dissociation constant between about 10^0 and 10^{-5} and wherein the soil being treated has an average particle size sufficient to pass through a 10 mesh screen but retained substantially completely on a 200 mesh screen.

3. A process for stabilizing water-permeable soil in order to render the same substantially water-impermeable comprising applying an aqueous dispersion of a hydrochloric acid catalyzed thermosetting urea-formaldehyde resin having a solids content of between about 25% and 35% by weight based on the total weight of the dispersion and having an initial viscosity between about 5 centipoises and 50 centipoises and curing said resin at ambient temperatures to a substantially water-insoluble thermosetting state, wherein said soil has a particle size sufficient to pass through a 10 mesh screen but retained substantially completely on a 200 mesh screen.

4. A process for stabilizing water-permeable soil in order to render the same substantially water-impermeable comprising applying an aqueous dispersion of an

ammonium bisulfate catalyzed thermosetting urea-formaldehyde resin having a solids content of between about 25% and 35% by weight based on the total weight of the dispersion and having an initial viscosity between about 5 centipoises and 50 centipoises and curing said resin at ambient temperatures to a substantially water-insoluble thermosetting state, wherein said soil has a particle size sufficient to pass through a 10 mesh screen but retained substantially completely on a 200 mesh screen.

5. A process for stabilizing water-permeable soil in order to render the same substantially water-impermeable comprising applying an aqueous dispersion of an aniline hydrochloride catalyzed thermosetting urea-formaldehyde resin having a solids content of between about 25% and 35% by weight based on the total weight of the dispersion and having an initial viscosity between about 5 centipoises and 50 centipoises and curing said resin at ambient temperatures to a substantially water-insoluble thermosetting state, wherein said soil has a particle size sufficient to pass through a 10 mesh screen but retained substantially completely on a 200 mesh screen.

6. A process for stabilizing water-permeable soil in order to render the same substantially water-impermeable comprising applying an aqueous dispersion of a sulfuric acid catalyzed thermosetting urea-formaldehyde resin having a solids content of between about 25% and 35% by weight based on the total weight of the dispersion and having an initial viscosity between about 5 centipoises and 50 centipoises and curing said resin at ambient temperatures to a substantially water-insoluble thermosetting state, wherein said soil has a particle size sufficient to pass through a 10 mesh screen but retained substantially completely on a 200 mesh screen.

7. A process for stabilizing water-permeable soil in order to render the same substantially water-impermeable comprising applying an aqueous dispersion of a phosphoric acid catalyzed thermosetting urea-formaldehyde resin having a solids content of between about 25% and 35% by weight based on the total weight of the dispersion and having an initial viscosity between about 5 centipoises and 50 centipoises and curing said resin at ambient temperatures to a substantially water-insoluble thermosetting state, wherein said soil has a particle size sufficient to pass through a 10 mesh screen but retained substantially completely on a 200 mesh screen.

8. A process for stabilizing water-permeable soil in order to render the same substantially water-impermeable comprising applying an aqueous dispersion of a sodium bisulfate catalyzed thermosetting urea-formaldehyde resin having a solids content of between about 25% and 35% by weight based on the total weight of the dispersion and having an initial viscosity between about 5 centipoises and 50 centipoises and curing said resin at ambient temperatures to a substantially water-insoluble thermosetting state, wherein said soil has a particle size sufficient to pass through a 10 mesh screen but retained substantially completely on a 200 mesh screen.

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