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(54) IMPROVEMENTS IN OR RELATING TO METHODS OF SEALING OR STABILIZING POROUS STRUCTURES OR FORMATIONS

(71) We, TAKENAKA KOMUTEN Co., LTD. of 27, Honmachi 4-chome, Higashi-ku, Osaka, Japan, a joint-stock company duly organized under the laws of Japan, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is performed to be particularly described in and by the following statement:—

This invention relates to a method for use in sealing or stabilizing a porous structure or formation and particularly, but not exclusively, to a method of filling the pores of a porous ground formation with a water impermeable, insoluble, solid material in order to reinforce the formation. The method according to this invention can also be used for sealing underground structures against water or gas leakage and in reinforcing the load bearing capacity of underground formations immediately surrounding piles or tie-back anchor rods.

In conventional methods of soil stabilization by chemical injection, a liquid obtained by mixing two or more reacting chemical components just before injection is injected into the ground, first to replace ground water with the chemical mixture, and then, with the reaction between the chemical components, water-insoluble solid substances are formed within the interstices between soil particles for the purpose of waterproofing or strengthening the soil. However, in such a method each chemical component in the chemical mixture starts a continuous "liquid to solid" transformation at the moment when the different

chemical components are mixed together, so this solidification takes place with no consideration of the time required for the chemical mixture to flow through the injection equipment into the ground. Therefore, when the speed of solidification of the liquid is high, difficulty is caused by the rapid increase in viscosity of the liquid, often causing gelation of the chemical which produces a plug near the outlet of the injection pipe thus preventing further permeation of unreacted liquid. This method is unsuitable because proper injection becomes impossible.

On the other hand, when the speed of solidification is slow, although it is possible to control the increase of viscosity in the injection equipment the chemical still remains fluid even after it has reached the expected location within the ground and its concentration will be diluted by the ground water thereby further delaying the solidification. On some occasions the chemical is carried away from the expected ground location by the flow of ground water resulting in the complete failure of the injection process.

In other words, the chemical composition used in conventional methods requires two fundamentally contradicting characteristics, that is, the maintenance of fluidity and rapid solidification. As to this mutual contradiction, the only known method of controlling the speed of solidification of the chemical is the extremely passive step of controlling the speed of chemical reaction so that the increase of viscosity is kept as low as possible during an

initial injection period but rapidly increases after a certain period of time. However the speed of the reaction is always influenced by the ambient temperature, the concentration of the chemicals, the ratio of chemical components, or the like, and control of the reaction is not only inherently difficult but there are also the complications which are always present in practice such as the necessity of selecting the optimum speed of solidification due to a consideration of ground conditions, the capacity of the injection equipment, the workmen's experience, etc. and this is the greatest cause of instability in the result of previous injection work.

That is to say, such a complicated method requiring a high degree of technical competence cannot be considered suitable for use by untrained personnel.

Also, in underground structures, such as basements or tunnels, leakage of ground water may occur through cracks in a concrete wall or lining. Conventionally, the water has been cut off at such locations by sealing the cracks with an injected chemical by a method similar to those referred to above. Such methods also had defects similar to those mentioned above. Even if solidification of the chemical liquid within the cracks was obtained, it would still be impossible to avoid the presence of water between the solidified substance and the surface of the crack, and this remaining water will cause imperfect contact between the solidified substance and the surface of the crack; also the permeation of this water within the said solidified substance will decrease the strength of it by a softening phenomenon thereby making perfect cut-off of water impossible.

Where it is required to construct underground anchors these are usually constructed by excavating in advance and constructing a concrete anchoring structure, or by boring holes in the ground which are then filled in with cement mortar together with anchor rods, thereby increasing ground stability. However, excavation or boring require large scale equipment, and in some cases neighbouring structures are sufficiently close to render such methods impractical. Further, excavation or boring require great amount of labour and time, and concrete or cement mortar requires a considerable time before they attain the required strengths, and such methods cannot be employed in cases where a landslide of retaining walls or a cut slope is foreseen and an urgent reinforcement is required.

In addition, in cases where the amount of ground water is great, or where an underground stream exists at the site of the proposed anchoring structure, the construction thereof not only required a great amount of labour and time, but at times it was impossible to obtain the originally desired strength.

When the conventional chemical injection method is used for soil stabilization the consolidated lumps of earth formed by the permeation of the injected chemicals are generally spherical or cylindrical in shape around the outlet of the chemical injection pipes and are solid and homogeneous. It is not necessary however for the lumps of earth to be solid and homogeneous for it will be more economical for them to be shells of earth whose peripheral surfaces only are solidified while the interior remains unsolidified. Furthermore, using conventional chemical injection methods it was almost impossible to produce cell-form or shell-form lumps of solidified earth.

This invention has been developed to improve the fundamental defects of the conventional chemical method, and in one embodiment chemical injection method, and in one embodiment there is employed a chemical liquid substance which includes an isocyanate group compound which upon coming into contact with water will start a chemical reaction where a water-insoluble solid substance is produced and gas is liberated.

The points at which this invention fundamentally differs from the conventional method in both theory and practice are:

(a) Not only that the chemical used will not produce solid substance unless the chemical itself comes in contact with water, but also that:

(b) Liberating gas while at the same time producing a solid substance is the most notable characteristic. Because of the gas pressure, the water insoluble solid substance produced in this method is forced under pressure into the pores or interstices of the ground which provides the porous structure or formation to complete the sealing.

(c) Also, the liquid substance which must be solidified by reacting with water in this invention remains in a fluid state so long as it does not encounter water. Therefore it will easily permeate into interstices or pores of the ground formation into which it is injected.

(d) If there is ground water present, it will produce a solid substance without causing the difficulty of an imperfect reaction due to dilution by the ground water. Liberated gas temporarily expels any excess ground water. And the effective area of the solidification in this method is broadly extended by means of the bubble of the gas.

(e) Changing into a form which cannot be carried away by water, filling the interstices or pores of the formation assuring the action of cutting off water and efficiently strengthening the ground.

(f) Furthermore, the work is very easy for there is no difficulty in controlling the speed of solidification.

(g) In other words, the liquid substance em-

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5 employed in this invention automatically reacts at locations where cutting off of water or where strengthening is required. Since this chemical automatically selects and reacts in water bearing ground or upon the location of a water leak, the desired work can be performed inexpensively and rationally without requiring the high technical experience which was necessary with conventional methods.

10 Also, only very simple injection equipment is required for the work, and no experience in the performance of work is required.

15 For instance, the prevention of water leakage at a sheet pile retaining wall in an underground excavation, or in tunnel excavation work, the prevention of collapse at tunnel facing work, the rapid stabilization of comparatively shallow muddy land, can all be simply effected by concentrated injections with a

20 piston type manual pump or a simple injection needle type plunger.

25 As is clear from the above, this invention does not require the speed of solidification of the chemical liquid to be controlled by the complicated and tiresome methods which were necessary in the conventional method.

30 From one aspect the invention provides a method for use in sealing or stabilizing a porous structure or formation including the steps of preparing a fluid substance comprising an isocyanate compound which, reacts with water to produce a water-insoluble solidified substance while liberating carbon dioxide gas, and a surface active agent which does not

35 react with said isocyanate compound but which facilitates association between the compound and water; said fluid substance itself not including any reactant that would cause its solidification, and introducing the said fluid substance into the porous structure or formation whereby the substance reacts with water present in the structure or formation to produce, in the said structure or formation, a water-insoluble solidified substance contain-

40 ing carbon dioxide gas.

45 The invention also provides a method for use in sealing or stabilizing a porous structure or formation including the steps of preparing a fluid substance comprising a mixture of an organic silane compound and a fine powdered carbide (which mixture reacts with water to produce a water-insoluble substance while liberating hydrocarbon gas) a solvent for the said organic silane compound, and a surface active agent which does

50 not react with the said organic silane compound but which facilitates association between the compound and water and serves to improve the stability of hydrocarbon gas bubbles liberated from the fluid substance, the fluid substance itself not including any reactant that would cause its solidification and introducing the said fluid substance into the porous structure or formation whereby the substance re-

55 acts with water present in the structure or

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formation to produce, in the said structure or formation, a water insoluble solidified substance containing hydrocarbon gas.

Various embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings, in which:—

Figure 1 is a simplified side view showing the case where this invention is utilized for soil stabilization;

Figure 2 is a partial sectional side view showing a chemical injection pipe for injection of chemical into the ground;

Figures 3 and 5 are enlarged partial sectional side views respectively showing the injection nozzles of different chemical injection equipment;

Figure 4 is a partial sectional side view showing chemical injection equipment which can be conveniently used in the injection of chemical into the ground;

Figure 6 is a longitudinal section showing cracks of a building, water leakage through which can be cut off by this method;

Figures 7 through 9 are side views of longitudinal sections showing the sequences of work in cutting off water from leaking cracks;

Figure 10 is a simplified side view illustrating the present invention employed in securing anchor rods in the ground;

Figure 11 is a side view of the outlet ends of a chemical injection pipe suitable for the case where the chemical injection pipes themselves are used as anchor rods or bearing piles;

Figure 12 is a longitudinal section showing the outlet end of another chemical injection pipe especially suitable for the case where the chemical injection pipe itself is used as an anchor rod;

Figure 13 is a perspective view of an underground water cut off wall constructed by the conventional method;

Figure 14 is a partially sectioned perspective view of a water cut off wall constructed utilizing the method of this invention;

Figure 15 is a partly sectioned perspective view of a solidified mass showing only the solids in stabilizing formation.

Referring now to Figures 1 and 2; an injection pipe 23 having a sharply pointed end 20 is perforated with great many chemical outlet holes 22, on the wall 21 which is, for example, as shown in Figure 1, driven to a certain predetermined depth into ground which requires stabilizing, such as the ground 25 which is adjacent the ground 24 which is scheduled for excavation. The head portion 26 of the injection pipe 23 and a chemical tank 27 are connected by a pipe 28; a liquid from the tank 27 is forced into the chemical injection pipe 23 under pressure applied by means of compressed air supplied by an air compressor 29 and thus it is injected into the ground 25 through each outlet hole 22.

The liquid substance to be used in this case

is one which, on contact with water, starts reacting to produce a water-insoluble solid substance in the pores or interstices between soil particles of the ground at the same time liberating a gas. This liquid causes the formation of a water-insoluble consolidated lump of earth 30 by a reaction with the water contained in the ground thereby strengthening the said ground. When the scheduled excavation of the ground 24 is carried out water seepage from the excavated surfaces is shut off by the water insoluble consolidated earth 30. In cases where the ground to be stabilized is very deep the injection outlet holes 22 on the injection pipe 23 may be provided along a length corresponding to the depth or the said chemical injection may be performed by gradually raising or lowering the injection pipe 23 while the liquid is being injected.

An example of the chemical liquid which can be used in the method according to the invention is an isocyanate compound which is expressed in the general formula $R-(NCO)_n$. Where R is an organic group of either an aliphatic or aromatic family or both and n is an integer of 2 or more. Another suitable group of compounds are reactive prepolymers obtained by the reaction between said isocyanate compounds and compounds containing active hydrogen. These prepolymers have unreacted isocyanate groups which can react with water coming into contact with the prepolymer. These prepolymer compounds react with water liberating carbon dioxide gas and polymerise producing a water-insoluble gel-form high polymer substance.

Thus these isocyanate compounds are polyisocyanates of aliphatic or aromatic family such as: 2,4-tolylene diisocyanate; 2,6-tolylene diisocyanate, a mixture of 2,4- and 2,6-tolylene diisocyanate, crude tolylenediisocyanate, diphenylmethane-4,4'-diisocyanate, polyallylene polyisocyanate, m-phenylene diisocyanate, hexamethylene - 1,6 - diisocyanate, o-, m & p-xylene diisocyanates, methylene bis - p-phenylene diisocyanate, and polyallylene polyphenyl isocyanates; and prepolymers containing an isocyanate-terminated group produced by the reactions of excess of these polyisocyanates (i.e. those listed at the beginning of this sentence) with compounds containing active hydrogen.

As compounds containing active hydrogen employed for the production of said prepolymers, mention may be made of water, alcohols, organic acids, amines, etc.; but for the alcohols, those of dihydric or other polyhydric alcohols are desirable, and such low molecular weight polyhydric alcohols as ethylene glycol, propylene glycol, diethylene glycol, glycerine, trimethylol ethane, trimethylol propane and pentaerythritol, together with castor oil and its derivatives, hydroxyl-group-terminated polyethers and polyesters are also to be included.

The said hydroxyl-group-terminated poly-

ethers are the addition polymerization products between the low molecular weight compounds containing active hydrogen and alkylene oxides, and in this case it is desirable to choose low molecular weight compounds containing at least 2 or more active hydrogen atoms per molecule. And for practical example of the aforementioned polyether, the reaction products obtained between low molecular weight compounds containing active hydrogen, which may be water, ethylene glycol, propylene glycol, glycerine, trimethylol propane, pentaerythritol sorbitol, cane sugar, phosphorous acids, orthophosphoric acid, glycerophosphoric and other phosphoric acids, ammonia, ethylene, diamine, diethylene amine, triamine, or urea etc; and also ethylene oxide, propylene oxide, 2,3-butylene oxide, tetrahydrofuran, epichlorohydrin, or styrene oxide, etc. which are one or more kinds of alkylene oxides may be named.

Among the hydroxyl group-terminated polyesters are the products obtained by the reaction between organic polybasic acids and an excess of polyhydric alcohols. The organic polybasic acid may be oxalic acid, succinic acid, adipic acid, azelaic acid, sebacic acid, maleic acid, maleic anhydride, fumaric acid, phthalic anhydride, isophthalic acid, terephthalic acid, tetrachlorophthalic acid, trimellitic acid and the like. The polyhydric alcohols may be ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, 1,3-butylene glycol, 1,4-butylene glycol, neopentyl glycol, 1,6-hexanediol, 1,3,6-hexanetriol, glycerine, trimethylol propane, trimethylol ethane, pentaerythritol, sorbitol and mixtures thereof. The polyesters may be modified by the addition of small amount of organic monobasic acids and monohydric alcohols. Further, the hydroxyl group-terminated polyesters produced by the polymerization of oxy-acids and those lactonic compounds are also useful. As to the organic acids, all the organic acids which are used for said hydroxyl-group-terminated polyesters are useful. Furthermore these hydroxyl-group-terminated polyesters which are produced from said organic acids and raw materials for the production of said hydroxyl-group-terminated polyethers can also be utilized.

As for the amines, all those containing primary or secondary amines within their molecules are usable. Mention may be made of ammonia, methyl amine, hydrazine, ethylene diamine, diethylene triamine, and amine-terminated polyamides. However, isocyanate-terminated prepolymers which are produced from amines and an excess of polyisocyanate generally lack stability to be stored and so they are not useful.

Preferably any isocyanate compound to be used in this invention is to be in a liquid state without water, however, if it is a solid which dissolves in a solvent, then it will serve the

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purpose just as well. Further, it is possible to adjust the viscosity of said liquid by suitably using solvents according to the condition of the soil to be injected at the site in order to maintain the appropriate viscosity for the work. Generally, the appropriate viscosity is 1—2000 cps, the desirable content of isocyanate group being 2% or more. The solvents used are those which have no groups reactive with the isocyanate group and which contain no water, including aromatic hydrocarbons, aliphatic hydrocarbons, ketones, esters, ethers and alkylhalides. As practical examples thereof, mention may be made of benzene, toluene, xylene, acetone, methyl-ethyl ketone, ethyl acetate, butyl acetate, cellosolve acetate, trichloroethylene, dichloromethane and dichlorobenzene.

When isocyanate compounds react with water contained in the ground, a suitable amount of catalysts and crosslinking agents may be added for adjusting the reaction. As catalysts, any suitable catalyst which accelerates the reaction of known isocyanates with compounds containing active hydrogen may be used. For instance, mention may be made of triethylamine, N-methylmorpholine, N-ethylmorpholine, N-cocomorpholine, dimethylbenzyl amine, triethylene diamine, N,N - dimethyl - 2 - methylpiperazine, pentamethyldiethylene triamine etc. of the tertiary amines or stannous chloride, dibutyl tin dilaurate, dibutyl tin oxide, stannous octate and other organo tin compounds. These catalysts may be used as mixtures thereof or may be suitably diluted with solvent and allowed to penetrate into the ground beforehand. Further, to improve the contact of said isocyanate compounds with water and thereby allowing their reaction

to proceed uniformly or to control the stability of the liberated carbon dioxide gas bubbles, surface active agents are added to the isocyanate compounds beforehand. The particularly useful surface active agents are silicone type non-ionic ones, which are useful in producing the well known urethane foam. 40 45

When additives such as mentioned above are added to said isocyanate compounds as may be required, and as the said isocyanate compound is injected into the ground, it will start the polymerizing reaction at the instant it comes in contact with ground water to produce water-insoluble gel-form high polymer solid substance within the pores or the interstices between soil particles resulting in an instantly effective stabilization of the ground without the accompanying defects of the conventional method which have been pointed out above. 50 55

The results obtained in experiments of the chemical injection methods of this invention are given below: 60

TEST 1

A model representing unstable ground and consisting of a sand layer in which the hydraulic gradient can be freely controlled was used. Comparisons were made between 4 kinds of representative grouts of water-soluble chemical liquids available on the market, meeting the conditions shown in the attached Table 1. The isocyanate type prepolymer used in this experiment consisted of 70 parts in weight of 2-functional urethane prepolymer of polypropylene glycol and tolylone diisocyanate, diluted with 30 parts in weight of xylene solvent, and into which a silicone-type surface active agent of 0.1% in total weight and triethylamine of 0.5% as catalyst were added. 65 70 75

TABLE 1. — CONDITION FOR TEST

Item	Exp't. 1	Exp't. 1	Expt'. 3
Grain Size of soil sample	0.3—0.6 mm	0.6—1.2 mm	1.2—2.5 mm
Porosity of soil sample	40%	38%	37.5%
Hydraulic gradient	1.5	1.5	1.5
Apparent velocity of water flow	0.600 mm/sec.	0.747 mm/sec.	0.800 mm/sec.
True velocity of water flow	1.50 mm/sec.	1.965 mm/sec.	2.130 mm/sec.
Coefficient of water permeability of soil sample	4.00×10^{-2} cm/sec.	4.98×10^{-2} cm/sec.	5.83×10^{-2} cm/sec.
Quantity of injection grout	300 ml	300 ml	300 ml
Injection pressure	0.5 kg/cm ²	0.5 kg/cm ²	0.5 kg/cm ²
Injection time	20—40 sec.	20—40 sec.	20—40 sec.
Gel-time	60 ± 5 sec.	60 ± 5 sec.	60 ± 5 sec.

The results of the experiments as shown in tables 2—4 inclusive.

TABLE 2. — RESULTS OF TEST 1

Type of Grout used	Consolidated Volume (cm ³)	(Consolidated Volume/Injected Qty. of Grout) × 100 (%)	Injection Efficiency: (Void Vol./Injected Qty. of Grout) × 100 (%)
Isocyanate-type Prepolymer	1.887	629.0	251.6
Acrylic amide type	572	124.0	49.6
Water-glass type	515	171.7	68.7
Urea-formaldehyde type	402	134.0	53.6
Chrome-lignin type	460	153.3	61.3

TABLE 3. — RESULTS OF THE TEST 2

Type of Grout used	Consolidated Volume (cm ³)	(Consolidated Volume/Injected Qty. of Grout) × 100 (%)	Injection Efficiency: (Void Vol./Injected Qty. of Grout) × 100 (%)
Isocyanate-type prepolymer	1,860	620.0	235.6
Acrylic amide type	279	93.0	35.0
Water-glass type	181	60.3	22.9
Urea-formaldehyde type	86	28.7	10.9
Chrome-lignin type	120	40.0	14.9

TABLE 4. — RESULTS OF THE TEST 3

Type of Grout used	Consolidated Volume (cm ³)	(Consolidated Volume/Injected Qty. of Grout) × 100 (%)	Injection Efficiency: (Void Vol./Injected Qty. of Grout) × 100 (%)
Isocyanate-type prepolymer	1,560	520.0	197.6
Acrylic* amide type	565	183.3	71.6
Water-glass type	330	110.0	41.8
Urea-formaldehyde type	295	98.3	37.7
Chrome-lignin type	295	98.3	37.7

(TEST 2.)

5 A model representing a ground formation of sandwich type was prepared in which a layer of sieved sand with grain size of 0.6—1.2 mm. was held between an upper and a lower impermeable clay layer; comparative experiments were made therewith for the sealing effect against water flow at the sand layer for 4 kinds of grout representative of water soluble chemical liquids available on the market and

the isocyanate-type prepolymer of this invention under the conditions shown in the attached Table 5. The isocyanate type prepolymer used in this experiment consisted of 70 parts in weight of 2-functional urethane prepolymer from tolylene diisocyanate and polypropylene glycol, diluted by adding 10 parts in weight of acetone and 20 parts in weight of xylene, into which triethylene diamine as 0.2% of the total weight is added as catalyst.

TABLE 5. — CONDITIONS FOR TEST

Porosity of soil sample:	38%
Hydraulic gradient:	3.0
Apparent velocity of water flow:	1.39 mm/sec.
True velocity of water flow:	3.66 mm/sec.
Injection method:	One shot method
Quantity of injected grout:	600 ml
Injection pressure:	0.5 kg/cm ²
Injection time:	15—30 sec.
Gel time:	45 sec.

The results of the experiment are as shown in table 6, and the isocyanate type prepolymer of this invention especially was the only case where the extent of consolidation showed a capability of completely cutting off flowing water and showing a cut-off efficiency of 100%.

TABLE 6. — RESULT OF WATER SHUT-OFF TEST

Type of Grout Used	Consolidated Volume (cm ³)	(Consolidated Volume/ Injected Qty. of Grout) × 100 (%)	Injection Efficiency: (Void Vol./ Injected Qty. of Grout) × 100 (%)	Efficiency of Water Shut-off *
Isocyanate-type prepolymer	4750	7917	300.8	100
Acrylic amide type	flowed away	—	—	—
Water-glass type	flowed away	—	—	—
Urea-formaldehyde type	760	126.7	48.1	7.15
Chrome-lignin type	555	92.5	35.2	14.7

$$* \text{ efficiency of water shut-off} = \frac{a - b}{a} \times 100$$

where a: Water flow rate before injection
b: Water flow rate after injection.

A liquid organic-silane compound given by the general formula $Rm-Si-X_{(4-m)}$ together with a small amount of fine metallic carbide suspended in the liquid can also be used in the method according to this invention; the liquid organic silane compound reacts with water to hydrolyze at normal temperatures to produce a water-insoluble gel-like silicone compound and said fine metallic carbide liberates hydrocarbon gas in contact with water.

In this case 'R' is an organic group of alkyl or aryl radical, and X is an alkoxy group or halogen atom.

In general the less carbon atoms R contains, the faster it hydrolyzes and the more its fluidity increases and therefore it may be effectively applied to this invention.

In the case where X is a halogen atom, its usage is confined to situations in which the corrosive effect due to liberated hydrogen halide may be ignored.

When X is an alkoxy group it is relatively cheap in cost and does not liberate any substances with corrosive properties but generally has a defect in that it is slow in hydrolysis. It is necessary, therefore, to take steps to accelerate the hydrolysis. The hydrolysis may be effectively accelerated by mixing with the silane a small amount of organic acid, or a suitable amount of alcohol in which sodium alcoholate is dissolved.

Those silanes which are particularly useful are alkoxy-silanes, such as of tetra-methoxy silane, tetra-ethoxy silane or the like. Those silanes which are crude products containing little remainder of hydrochloric acid are rather cheap and more speedy in hydrolysis than the refined products, so they are suitable in practice.

As the fine metallic carbide compounds suspended in the liquid as mentioned above, calcium carbide or magnesium carbide may be used to react with water to produce hydrocarbon gas.

When a lot of gas bubbles is desired, as it is for some purposes, it will be achieved by increasing the quantity of these fine metallic carbide particles suspended in the liquid.

In this case the addition of a carbide which hydrolyzes to produce calcium hydroxide has the effect of accelerating the hydrolysis of the said organic silane compounds due to its alkalinity.

With reference to Figure 3 the installation of a check valve system 33 at an outlet end 32 of an injection pipe 31 which is to be used for the injection of one of the above described chemical liquids into the ground is particularly desirable for the following reasons:

The presence of a check valve prevents the following three phenomena at the time of injection;

(i) the back flow of the chemical liquid in the injection pipe resulting from the back pressure towards the chemical tank by the

artesian pressure of underground water,

(ii) the back flow of chemical liquid due to increase in underground pressure from continuous injection of the liquid chemical,

(iii) the back flow of chemical liquid due to increase in underground pressure caused by the gas liberated by the said isocyanate or organic-silane compounds injected into the ground so that under any conditions, smooth and efficient chemical injection can always be performed.

Further, with the pressure of the gas produced by the injected liquid chemical and with the provision of the check valve acting as a backwood force resisting point, the injected chemical liquid actively spreads into the ground, thus enlarging the reinforced or water proofed region.

As shown in Figure 4 a chemical injection equipment 40 comprises a liquid chemical injection pipe 38 which is connected to a closing cock 37 which is connected to a pressure chamber 36 of a manual injection instrument-type pump 35, and a manual piston 39 by the operation of which the chemical liquid stored in said pressure chamber 36 can be injected under a suitable static pressure. This is useful as a handy equipment for effective performance of emergency works at job sites.

It is also desirable to install an anti-back-flow system such as described in relation to the embodiment described with reference to Figure 3.

As shown in Figure 5, a chemical injection pipe 45 has an open end to serve as an outlet, for which a cap 50 is provided,

The cap 50 is to bear upon the outlet 46, and has a peripheral portion 48 extending radially beyond the outer surface of the pipe 45, and a sharply pointed forward end 49. The said injection pipe 45 is driven into the ground to a depth previously determined, then by pulling out slightly said injection pipe 45 the projecting peripheral portion 48 of the cap acting as resistance, the said cap 50 will be left at the driven position so that the chemical injection outlet 46 will open. With this system prepared in advance the plugging of the injection outlet end by earth can be prevented when driving the injection pipe into the ground; and moreover, it will be useful in spreading the injected liquid chemical in the horizontal direction.

Such a cap and the anti-back-flow mechanical system as described in relation to Figure 3 when combined will provide a surer and better performance in injection of the chemical liquid.

The method of this invention can be extensively used not only to stabilize and strengthen the ground, but also to seal porous formations such as occur between concrete linings and the earth in tunnels, cracks in exterior walls of a basement, or spaces caused by the separation of finishing cement mortar from structural concrete. They can be sealed to prevent leakage of

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- water through said spaces and sealing off there-
of can be effectively performed. For example,
as shown in Figure 6, cracks 58 formed in an
exterior concrete wall 56 or a separated portion
5 60 between the exterior concrete wall and
finish cement mortar 59 which are liable to
cause or are actually causing ground water
leakage from the outside into the interior can
be effectively treated.
- 10 Also, it can be effectively applied to seal
leaking cracks in tunnel or water tank walls, for
example, as shown in Figure 7, a V-cut 62
is made along a crack portion 61 the front sur-
face of which is exposed and as shown in
15 Figure 8 quick setting mortar 63 prepared just
beforehand is filled into said V-cut, then, as
shown in Fig. 9 chemical injection holes 64
reaching the interior of cracks are made at
suitable locations, and the required amount of
20 chemical liquid is injected through said in-
jection holes 64 by means of a piston type
manual pump or a simple plunger equipment
with nozzles 65 which fit into said injection
holes 64. The chemical liquid, by the inner
25 pressure exerted by the liberated gas, will au-
tomatically fill the inside of the cracks from end
to end to form solid substance 66, and thus the
purpose of sealing off or shutting off of water
is accomplished.
- 30 Further, if in this case, the liquid chemical
is used in the mortar 63, the mortar so ob-
tained will be more effective. Namely, this
mortar even with the presence of water at the
portion of V-cut 62 will set with no trouble,
35 and a good bond can be obtained between
the interior surfaces of the V-cut and this
mortar. Further, due to the gas pressure origi-
nated within this mortar, the mortar is forced
against the interior side of the V-cut leaving
40 no unbonded parts and resulting in ideal filling.
The presence of water will obstruct the setting
of more usual mortar, so for such purposes al-
most no good effect can be expected from
them. Further, the solidified substances pro-
45 duced by the injection chemical liquid will
remain not only within the interstices and
pores of the structures but they can be ex-
tended into the outside ground as well, cutting
off the water more effectively. Also, as an-
50 other useful method of cutting off water leak-
age from cracks in structures the wall surfaces
with cracks can be chipped back slightly, the
solidifying substance is then applied to the
cracks and finished by trowelling or packing.
55 This method is particularly effective for such
locations where cracks in the form of a single
line are not clearly visible and for locations of
seeping water leakage.
- 60 To the chemical liquids referred to above,
sand, powdered glass, carbon powder, hy-
draulic cement, or other fine substances can be
mixed to produce a paste-like mortar, and
by utilizing this mortar water cut-off can be
completed at the stage shown in Figure 8. In
65 this case the amount of catalyst added may
be adjusted to control the setting speed. Again,
to have sufficient water on the interior surfaces
of the V-cut it is desirable to spray water over
them beforehand.
- Further, since it takes longer for the leaking
70 water to react upon the front surface of the
filling substance, the proper plasticity for
trowelling can be maintained for a sufficiently
long period, so it also has the advantage of
75 allowing more time to finish the built-up sur-
face so as to be smooth and flush with the
existing surrounding surfaces.
- By the addition of aggregate to the said
chemical liquid a paste-like mixture as in the
use of cement mortar can be obtained, but an
80 effect which was not obtained by the use of
cement mortar may be obtained; that is, the
packing substance itself can be kept in a state
of optimum consistency for handling and pack-
ing and it is also possible to cut off the water
85 immediately by the almost instantaneous solid-
ification of the filling substance.
- Also since these chemical liquids liberate
gas at the time of polymerization in contact
with water, it can be well understood from the
90 foregoing explanation that accurate and effec-
tive water sealing can be obtained.
- Further, the locations of water leakage to
which this method can be applied is not limited
95 to those of underground structures only, but
also to those of water tank walls, retaining
walls, bank surfaces etc.
- This method of sealing off of water will be
described in the following example.
- Three years and five months after construc-
100 tion cracks occurred in the foundation slab of
a reinforced concrete building which was lo-
cated on a sandy-gravel strata 13 meters below
the ground water level. The crack was ap-
proximately 1 mm. in width and approxi-
105 mately 3.5 meters in length and the water
leakage was about 150 l/minute. With the in-
tention of sealing off this seepage of ground
water with great pressure, three holes ap-
proximately equal distances apart from each
110 other were bored into the foundation slab
along the crack, and into each of the bored
hole a chemical liquid injection pipe equipped
with a cap with pointed end as shown in Figure
5 and an anti-back-flow mechanism as shown
115 in Figure 3 was inserted placing the pointed
end of each pipe at a position approximately
20 cm. deep in the ground. Approximately 80
liters of chemical liquid consisting of iso-
cyanate type prepolymer was injected through
120 each chemical injection pipe.
- As a result of the injection approximately
10% of the total amount of the chemical
liquid came out from the crack and flowed over
the foundation slab, while most of the remain-
125 ing chemical liquid filled the crack and the
ground below and solidified. The amount of
water leakage through the crack decreased to
approximately 2 l/minute. Further, a partial
V-cut was made where the sealing off was im- 130

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perfect, and as shown in Figure 9 chemical liquid injection holes were prepared and at the same time the portions around the V-cut were filled with quick setting mortar; through the said chemical liquid injection holes a total amount of 1 litre of the chemical liquid consisting of the said isocyanate type prepolymer was injected with a simple manual injection type pump as shown in Figure 4 stopping completely the leakage of water through the crack. The chemical liquid isocyanate type prepolymer used in this case was the same as that used in the second experiment described with respect to the first embodiment of this invention and the quick setting mortar used in packing consisted of 1 part by weight of this isocyanate type prepolymer, 3 parts by weight of sieved river sand with an average grain size of 0.1—0.3 mm. and 0.4 part of water. This was used when desirable workability had been obtained by mixing the components together.

The method according to this invention can also be applied to the construction of piles or tie-back anchor rods.

Figure 10 illustrates an example of an earth retaining (or tie-back) anchor for the face of a cut slope face, where three injection pipes 72 which have a number of chemical injection outlet holes 71 drilled at fixed points along a part of their length have been driven to a predetermined depth. They are one by one coupled to a connecting hose 75 which is connected to a tank 74 containing as mentioned with respect to previous embodiments, a chemical which, upon contact with water reacts to produce a water-insoluble substance. This chemical is forced into the injection pipe 72 under static pressure supplied by an air compressor 76 and passes through the chemical outlet holes of the said pipe. The chemical is thus injected into the ground 77 and reacts on contact with ground water contained in said ground to produce a large bulb-shaped consolidated lump of earth 78 around the chemical outlet portion 71 which will resist attempted removal of the pipe 72.

The number and the diameter of chemical outlet holes 71 can be determined from the optimum conditions in consideration of the geological conditions of the ground, the desired shape and size of the bulb type consolidated lumps of earth, the viscosity resistance of the chemical liquid, and allowable stress of the cross section of the injection pipe.

By making possible the injection from the extremity of the injection pipe by using a cap as shown in Figure 5, it is possible to produce consolidated lumps of earth which can increase the bearing power. It is also possible to use the injection pipe as a bearing pile. In this case the preparation of injection outlets on the sides of the injection pipe will be effective for further increasing the bearing force, and it is of course possible that the consolidated lumps of

earth produced by the side outlets alone will sufficiently increase the bearing power of the pile.

As mentioned above, when the invention is to fix the pipe in the ground, the pipe with chemical outlet at the end will be driven into the ground and the chemical liquid which produces the water-insoluble solidified substance will be injected thereby producing a bulb-like or generally cylindrical consolidated lump of earth without the accompanying conventional defects as described earlier. Anchors of all types having great pull-out resistance can easily and quickly be constructed by this method. For example, anchors of retaining walls, bridge piers, anchors for grate-form retaining walls for rock bores, for a land-slide zone, or a cut-slope face; anchors to be constructed for stabilizing foundations of structures receiving horizontal forces such as wind pressure or earthquake, or piles with increased point bearing capacity can all be constructed by this method.

In the use of the conventional two-liquid type injection chemical liquids, the chemicals are liable to flow away without concentrating around the pipe so effective formation of bulb-like consolidated lumps of earth cannot be expected, while in the cases of this invention the chemical liquid flowing out of the pipe reacts with the ground water immediately on leaving the said pipe and at this position the bulb-like consolidated lumps of earth are formed. By filling the cracks and pores in the ground around the anchors with the consolidated substance the weaker portions of the ground are rapidly strengthened. Therefore it is possible to prevent unexpected accidents occurring from the lowering of strength due to unknown uneven formations of the ground.

Further, and for the following reasons, the pull-out shearing resistance between an anchor-rod and its associated bulb like consolidated lump of earth is extremely large.

In anchors obtained by the method of this invention there exist the usual mechanical frictional forces governed by the angle of friction and the normal pressure which bears a relation with the pressure exerted between the bulb-like consolidated lump of earth and the lateral face of the anchor rod due to the pressure of the ground above. Also an extremely large bonding force is developed between the surface of the solid substance and that of the anchor-rod due to the adhesion action by the chemical injection liquid, and further, since a high polymer solid substance is continuously being formed through the injection chemical outlet holes of the injection pipe (or the anchor-rod) between the zones around the injection pipe and the interior of the injection pipe a riveting effect at the chemical outlet holes is obtained and so by these effects an extremely great pull-out shearing resistance is produced

between the bulb-like consolidated lumps of earth and the anchor rod.

5 Anchors constructed by the method of this invention can instantly produce the required strength, so in the case of emergency it can begin to work as an anchor immediately, since the chemical liquid used reacts as soon as it comes in contact with water to solidify and harden; whereas almost all of the solidified substances produced with the conventional water-soluble injection chemicals such as sodium aluminate, water glass, urea resin, phenol resin, acrylic-amid, chrome-lignin or the like have defects of swelling, softening and lowering of strength in the presence of ground water. Compared to these the chemicals of this invention have the advantage of becoming stronger in the presence of ground water.

10 It is of particular importance that the chemicals used in this method when in contact with water will liberate gas as well as producing water-insoluble substances. The liberation of gas causes the ground to be forced against the peripheral surface of the injecting pipe at right angles to the axis of the pipe so that so called radial pressure is created. This increases the bond between the ground and the pipe; at the same time however pressure in all directions is increased, and this together with the increase in the volume of consolidated lumps of earth creates an extremely great shearing resistance against pulling-out so the construction of a very strong anchor is possible.

15 A description of an experiment in which the method of this invention is performed for the case of a pull-out resisting pile i.e. an anchor is as follows:

(EXPERIMENT 1)

20 Two kinds of sand, one sieved to a grain size of 0.6—1.2 mm. and the other Toyoura standard sand meeting Japanese Industrial Standard R5201 (1964) were respectively water-compacted in a mould normally used in making 300 mmφ × 500mm. concrete test pieces. A steel pipe 17.3mm. in outer diameter with chemical injection outlet holes 1 mm. in diameter with a pitch of 1.5 cm. drilled in portion of the pipe 7.5 cm. from the end was driven into each of the compacted sample sand to a depth of 15 cm. To a prepolymer with NCO content of 25% produced by the reaction between polypropyleneoxide-triol with an OH value of 300 and an 80:20 mixture of 2,4- and 2,6-tolylene diisocyanate, 20% (of the prepolymer) of xylene was added as a diluent to form a homogeneous liquid, and 2% (of the liquid) of triethylamine was added as a catalyst. The mixed liquid was injected from the end of each steel pipe and 20 hours later they were removed from the mould and subjected to water immersed curing. After aging for 3 days pull-out tests of the steel pipes were made, and the results showed that for the sand of 0.6—1.2 mm. grain size yielding occurred

at 1012.5 kg. and for Toyoura standard sand at 1437.8 kg. Thus very high pull-out shearing resistances of 12.5 kg/cm² and 17.75 kg/cm² respectively were obtained.

(EXPERIMENT 2)

25 A number of 4.8 meters long 1 in. diameter gas pipes were driven to a depth of 4.5 meters at right angles to a 45° slope cut face, and the mixture of the prepolymer used in Experiment 1 diluted with 10% of xylene and 1% of the triethylamine injected. At the chemical injection outlet end (bulb-form portion) of each injection pipe was a sandy gravel layer containing a large amount of gravels of grain size approximately 50—100 mm. mixed therein. In this case the chemical outlet portion of the injection pipes were bored with 3 mm. diameter outlet holes at a pitch of 5 cm. staggered in 2 rows, for one 25 cm. and for the other 55 cm. from the lower end. For pipes with bored length of 25 cm., 3 kg. and 12 kg. of chemicals were injected and for pipes with bored length of 55 cm. 6 kg. and 24 kg. of chemicals were injected and pull-out test in the axial direction of the pipes were made. For comparison purposes pipes with no chemicals injected were also tested. The result of this test showed that the yield points for no chemical injection were below 0.5 tons, while for 3 kg. chemical injection the yield point was 3 tons, for 6 kg. 5.6 tons, for 12 kg. 6.0 tons and for 24 kg. 8 tons.

30 A helical projection or helical grooves provided on the injection pipe will give a rotating motion to the said pipe making not only the driving of same into the ground easier, but will also become effective by increasing the pull-out resistance. Such a helical projection or groove can be made on an end portion or on an intermediate portion of the injection pipe. However, the provision thereof on the peripheral surface where the chemical outlet holes are provided will cause better bonding between the consolidated lumps of earth and said helical projection or groove obtaining a much more desirable result.

35 As shown in Figure 11, if the outer diameter of portion 82, where outlet holes 81 of an injection pipe 80 are bored, is made smaller than that of the other portion of said pipe, it will be possible not only to decrease the tendency of the holes to become plugged with earth and decrease the resistance to the driving of said pipes into the ground, but it also will be useful in making the bonding force of consolidated lumps of earth with the injection pipe 80 stronger, and so this will be effective where as described in relation to the embodiment of Figure 10 the injection pipe itself is utilized as an anchor-rod or as a bearing pile.

40 In Figure 12 there is shown a modified construction of the end of an injection pipe where an injection pipe 93 which has a chemical outlet portion 92 with a number of chemi-

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cal outlet holes 91 is drilled at fixed points along a predetermined length near a cone shaped end part 90 the outlet holes 91 being inclined in such a way that their axial directions towards the interior make an acute angle θ with the driving direction of the injection pipe 93.

In using this type of injection pipe, even if a certain amount of earth enters the outlet holes while the pipe is being driven in, the percussion of the pipe driving will force the earth particles out according to the Law of Inertia, so that the plugging of said holes with earth will be considerably decreased, and discharge of chemicals in both circumferential and axial directions of the pipe within the expected zones will be more nearly as expected from the number of holes provided in the pipe. Also it will be easier to obtain consolidated lumps of earth in the initially expected shape and size, and in the case where the intention is to use the injection pipe itself as a tie-rod this modification will be helpful in increasing the pull-out resistance.

On the other hand the conventional type of injection pipes to be driven into the ground have injection outlet holes with axes at right angles to the surface of the injection pipe, so that in driving it is difficult to prevent earth from being trapped in and readily plugging up the holes. Occurrence of this plugging not only decreases the number of outlet holes; but also prevents chemicals from permeating to the expected zones in the ground, so that the initially expected consolidation will not be attained. As referred to previously, in the methods where the injection pipe itself is utilized as a bearing pile, the quantity of inside and outside connections of said pipe with the solidified substance which is an important functional element in increasing the pull-out or push-in shearing resistance, (the so-called riveting effect) will be described so that it will become difficult to obtain anchors or piles with initially expected resistance to pull-out forces or bearing power.

The use of the injection pipe as described in the embodiment shown in Figure 11 is effective in solving the difficulties as mentioned above.

The use of such injection pipes, as described in the embodiment shown in Figure 10 are of course effective in solving these difficulties. However, from the viewpoint of manufacturing injection pipes the type described with reference to Figure 11 is preferred.

This invention may also be applied to the construction of underground structures which can be effectively used as water cut-off walls, known sometimes as "curtains".

The construction by conventional chemical injection methods of a water cut-off wall in the form of a continuous row of subterranean "columns" consisting of consolidated earth as shown in Figure 13, when viewed from the purpose of cutting off of water the actual effec-

tive zone is the zone 95 which is shown hatched. The zone 96 without the hatching is constructed just as a matter of convenience during construction and is not functionally necessary, and so, in the zone 96 the chemicals which were used were wasted. In order to economize on the amount of chemicals used the spacing of injection pipes is made closer and at the same time the radius of the "columns" of consolidated earth is made smaller. However in this case more injection pipes 97 must be used so that some form of economical disadvantage cannot be avoided. If the radius of each "column" of consolidated earth is made smaller, then in constructing a water cut-off wall to a great depth, there is a tendency for the installed injection pipe 97 to shift away from the proper position resulting in difficulties in the construction of the continuous water cut-off wall.

By using injection chemical liquids which in contact with water produce a water-insoluble solid substance and at the same time liberate a gas, it is possible to form cell-like consolidated lumps of earth. In this case the chemical liquid is first injected into the ground through an injection pipe. When the chemical starts to react with ground water, and before gelation starts, so that the fluid condition is still maintained, a suitable amount of water or other liquid is injected through the same injection pipe. By such a 2-step injection method, the chemical first injected will be forced out some distance from the outlet of the injection pipe by the injection of the second fluid, and as a result it is possible to produce in the ground cell-like structures of consolidated earth in which the interior is not consolidated but comprises the same material as surrounds the cell-like structures. In this case because the central part of the consolidated lumps of earth has not come in contact with the ground water there is a tendency for the consolidation of the inner face to be delayed. However, if water is used for the liquid which is to be injected later, while the outer side of the said cell like consolidated lump of earth is in contact with the ground water, the inner or central portion of said lumps of earth will come in contact with the injected water, so with both the inside and outside of said consolidated lumps of earth being in contact with water there is the advantage of a quick consolidation. If a catalyst which can accelerate the chemical reaction of the injected chemical liquid were added in a small amount to the water to be used as a second injection fluid the consolidation from the interior will be accelerated. Further, since injected chemicals consisting of isocyanate type compounds are used, the reaction between the chemicals and the later injected water will naturally liberate carbon dioxide gas, then under the pressure exerted by this gas the chemical injected first will be automatically pushed outwardly so that

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with no extra work the zone of consolidation will be enlarged.

5 In general, an injected chemical liquid consisting of isocyanate type compounds is better than conventional injection chemicals because it produces a mechanically strong consolidated lump of earth or it effectively cuts off the ground water. But because of the high cost for practical use there are still problems. However, 10 by making effective use of the characteristics inherent in the isocyanate type compounds it is possible to make use of these liquids in an economical and inexpensive manner.

15 Figure 14 shows a multi-stage injection method in which an injection operation is repeated in a vertical direction by forming in turn cell-like consolidated lumps of earth 98 and constraining continuously a column from consolidated lumps of earth 99. By connecting 20 a number of these columns of consolidated lumps of earth 99 together a honeycomb-like construction forming a wall 100 is achieved.

25 In the upper part of the reference drawing the zones 101 and 102 which are shown horizontally encircled with dotted lines constitute a double row wall structure resulting in an effective water cut-off "curtain". Further, the front and back walls of zones 101 and 102 are reinforced by mutual connection at the zone 30 103, so it is very strong and can be utilized as an underground water cut-off curtain with high dependability.

35 From the fact that this is a curved shell-like consolidated lump of earth and that there is soil contained in the interior of the cell-like portion the amount of solidifying material required to construct the walls was very small and if, even a number of years after the construction of the curtain, the earth pressure 40 should rise causing a greater pressure between inside and outside of the structure it is nevertheless capable of maintaining an effective and strong condition. Construction is also very easy and economical requiring no excavation nor 45 pile-driving of ready-made piles which require an enormous amount of energy. In the process of its construction the chemicals form the cell-like structural body only by causing them to penetrate into the ground balanced 50 by earth pressure. As the cell-like body itself is formed in a condition which is not necessary to have a strength enough to cope with the earth pressure on the outside of said body until it has been formed its construction is very 55 easy.

Because of this, any underground structure constructed by this invention can also be utilized in increasing bearing strength (for both vertical and horizontal loads).

60 The method of constructing such an underground structure has been already explained. However, a particular mention may be made of the fact that the liquid which pushes and spreads the chemicals outwardly is preferably 65 a liquid that can accelerate the solidifying re-

action of said chemicals, and that even if this liquid is other than water, the solidifying chemical and this liquid must be alternately supplied into the injection pipe 97 through two separate pipes, connected to the injection pipe 97 with a valve.

70 In the excavation work of a shield having an inner diameter of 3 meters for the installation of a sewer culvert under a city street, an experiment was performed for the purpose of stabilizing a cutting face composed of a sandy stratum liable to collapse due to a large amount of ground water. A honeycomb-type under- 75 ground structure composed of continuous cell-like consolidated lumps of earth was formed. In this experiment at the ground located in front of the shield excavation a number of chemical injection pipes were driven into the ground at a intervals of 80 cm. in a grating- 80 like pattern, and by using these injection pipes a multiple-stage injection process was carried out and a honeycomb structure was constructed under the ground, as if to cover the front side of the cutting face, as shown in Figure 15. 85 In this case, each stage was 1.2 meters above the preceding stage and 40 liters of injection chemical liquid composed of an isocyanate type prepolymer was first injected and directly followed by the injection of 50 liters of water 90 through the same injection pipe to spread by pushing the first injected chemical to a wider zone. This operation was repeated for each 95 stage in turn, so that the cell-like consolidated lumps of earth were connected in the front-and-back, left-to-right, and in up-and-down directions. 100

The honeycomb underground structure thus formed stabilized the cutting face, and showed a suitable strength without causing difficulties 105 in excavation. A perfect water cut-off was achieved, and this made the shield excavation extremely safe and easy. The injection chemical liquid used for this case was composed of 70 parts in weight of 2-functional modified urethane prepolymer of polypropylene glycol 110 and tolylene diisocyanate modified with hydrocarbon resin, and diluted by adding 30 parts in weight of xylene; the NCO content was 18.5% and viscosity at 20°C 16.7 CPS. To this, triethylamine as 0.5% of total amount was 115 added as reaction accelerating catalyst. The water injected following the chemical injection was common fresh water to which 0.1% triethylamine was added as hardening accelerator. 120

In the embodiment described in relation to Figure 13 the solidified substances formed in a formation were composed of independent 125 shells each having an unsolidified portion there-within. Such structures are very effective in serving as water cut-off walls. But when the solidified structures are only for the purpose of strengthening the ground the unsolidified portions may be interconnected with each other that is, interconnected through openings in the walls between adjacent unsolidified portions. 130

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To strengthen formations as shown in Figure 15 the shells may be successively formed in three directions. At 110 in the figure is shown a part of the solidified shells, the un-solidified portions surrounded with the shell are shown at 111 and 112. They are in fact formed in irregular shapes.

Some of the practical embodiments of this invention have been described and explained with drawings. They are methods to which many changes can be made, and it must be understood that this invention is not limited only to those practical embodiments. Moreover, the mixtures described in the practical examples, unless they are contradicting, can be mutually interchangeable or can be combined into any combinations.

WHAT WE CLAIM IS:—

1. A method for use in sealing or stabilizing a porous structure or formation including the steps of preparing a fluid substance comprising an isocyanate compound which, reacts with water to produce a water-insoluble solidified substance while liberating carbon dioxide gas, and a surface active agent which does not react with said isocyanate compound but which facilitates association between the compound and water, said fluid substance itself not including any reactant that would cause its solidification, and introducing the said fluid substance into the porous structure or formation whereby the substance reacts with water present in the structure or formation to produce, in the said structure or formation, a water-insoluble solidified substance containing carbon dioxide gas.

2. A method for use in sealing or stabilizing a porous structure or formation as claimed in claim 1 wherein the fluid substance is prepared by dissolving the isocyanate compound in a solvent.

3. A method as claimed in either claim 1 or claim 2 which further includes the step of introducing a catalyst or cross-linking agent into the structure or formation to adjust the reaction of the compound.

4. A method for use in sealing or stabilizing a porous structure or formation including the steps of preparing a fluid substance comprising a mixture of an organic silane compound and a fine powdered carbide (which mixture reacts with water to produce a water-insoluble solidified substance while liberating hydrocarbon gas), a solvent for the said organic silane compound, and a surface active agent which does not react with the said organic silane compound but which facilitates association between the compound and water

and serves to improve the stability of hydrocarbon gas bubbles liberated from the fluid substance, the fluid substance itself not including any reactant that would cause its solidification, and introducing the said fluid substance into the porous structure or formation whereby the substance reacts with water present in the structure or formation to produce in the said structure or formation, a water insoluble solidified substance containing hydrocarbon gas.

5. A method as claimed in claim 1, 2 or 3, wherein said surface active agent is a silicone-type non-ionic surface active agent.

6. A method as claimed in any one of claims 1 to 3 or claim 5, wherein said fluid substance contains a catalyst which accelerates the reaction between said isocyanate compound and water.

7. A method as claimed in any preceding claim, wherein said fluid substance is mixed with fine grained solid particles.

8. A method as claimed in any preceding claim, wherein said fluid substance is mixed with hydraulic cement powder.

9. A method as claimed in any preceding claim, wherein after said fluid substance has been introduced into the structure or formation a fluid is introduced therein which causes the substance to spread out while maintaining its fluidity, said fluid serving to urge said fluid substance to move away from its position of introduction in the structure or formation and said fluid substance being then allowed to solidify by the agency of water, thereby producing a consolidated body shell or cell shape in the structure or formation.

10. A method as claimed in claim 9, wherein the fluid for causing said fluid substance to be moved in the structure or formation is a liquid having the function of solidifying said fluid substance.

11. A method as claimed in any preceding claim, characterized by inserting a pile in pipe form into the structure or formation introducing said fluid substance through an inner hollow space in the pile and a hole in the said pile and leaving said pile in position while said fluid substance solidifies to form a solid foundation for an anchor-rod or a bearing-pile.

12. A method for use in sealing or stabilizing a porous structure or formation substantially as hereinbefore claimed and described with reference to the accompanying drawings.

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To strengthen formations as shown in Figure 15 the shells may be successively formed in three directions. At 110 in the figure is shown a part of the solidified shells, the un-solidified portions surrounded with the shell are shown at 111 and 112. They are in fact formed in irregular shapes.

Some of the practical embodiments of this invention have been described and explained with drawings. They are methods to which many changes can be made, and it must be understood that this invention is not limited only to those practical embodiments. Moreover, the mixtures described in the practical examples, unless they are contradicting, can be mutually interchangeable or can be combined into any combinations.

WHAT WE CLAIM IS:—

1. A method for use in sealing or stabilizing a porous structure or formation including the steps of preparing a fluid substance comprising an isocyanate compound which, reacts with water to produce a water-insoluble solidified substance while liberating carbon dioxide gas, and a surface active agent which does not react with said isocyanate compound but which facilitates association between the compound and water, said fluid substance itself not including any reactant that would cause its solidification, and introducing the said fluid substance into the porous structure or formation whereby the substance reacts with water present in the structure or formation to produce, in the said structure or formation, a water-insoluble solidified substance containing carbon dioxide gas.

2. A method for use in sealing or stabilizing a porous structure or formation as claimed in claim 1 wherein the fluid substance is prepared by dissolving the isocyanate compound in a solvent.

3. A method as claimed in either claim 1 or claim 2 which further includes the step of introducing a catalyst or cross-linking agent into the structure or formation to adjust the reaction of the compound.

4. A method for use in sealing or stabilizing a porous structure or formation including the steps of preparing a fluid substance comprising a mixture of an organic silane compound and a fine powdered carbide (which mixture reacts with water to produce a water-insoluble solidified substance while liberating hydrocarbon gas), a solvent for the said organic silane compound, and a surface active agent which does not react with the said organic silane compound but which facilitates association between the compound and water

and serves to improve the stability of hydrocarbon gas bubbles liberated from the fluid substance, the fluid substance itself not including any reactant that would cause its solidification, and introducing the said fluid substance into the porous structure or formation whereby the substance reacts with water present in the structure or formation to produce in the said structure or formation, a water insoluble solidified substance containing hydrocarbon gas.

5. A method as claimed in claim 1, 2 or 3, wherein said surface active agent is a silicone-type non-ionic surface active agent.

6. A method as claimed in any one of claims 1 to 3 or claim 5, wherein said fluid substance contains a catalyst which accelerates the reaction between said isocyanate compound and water.

7. A method as claimed in any preceding claim, wherein said fluid substance is mixed with fine grained solid particles.

8. A method as claimed in any preceding claim, wherein said fluid substance is mixed with hydraulic cement powder.

9. A method as claimed in any preceding claim, wherein after said fluid substance has been introduced into the structure or formation a fluid is introduced therein which causes the substance to spread out while maintaining its fluidity, said fluid serving to urge said fluid substance to move away from its position of introduction in the structure or formation and said fluid substance being then allowed to solidify by the agency of water, thereby producing a consolidated body shell or cell shape in the structure or formation.

10. A method as claimed in claim 9, wherein the fluid for causing said fluid substance to be moved in the structure or formation is a liquid having the function of solidifying said fluid substance.

11. A method as claimed in any preceding claim, characterized by inserting a pile in pipe form into the structure or formation introducing said fluid substance through an inner hollow space in the pile and a hole in the said pile and leaving said pile in position while said fluid substance solidifies to form a solid foundation for an anchor-rod or a bearing-pile.

12. A method for use in sealing or stabilizing a porous structure or formation substantially as hereinbefore claimed and described with reference to the accompanying drawings.

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