

PATENT SPECIFICATION

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NO. DRAWINGS

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Int. Cl.:—C 01 b 33/32

COMPLETE SPECIFICATION

Gelling Silicates

We, PROGIL, a French Body Corporate of 77 Rue de Miromesnil, Paris 8, France, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to gelling alkali metal silicates, and to the use of such gelled silicates for consolidating and stabilizing soil.

It is known that by adding certain organic reagents to alkali metal silicates, silica gels may be obtained which are capable of changing to a solid mass having the characteristics of a cement. Numerous reagents have already been recommended for this purpose, e.g. fatty acids, phenols, esters of organic monoacids such as ethyl acetate, amides of aliphatic acids such as formamide (see, for example British Specification No. 910,450), alkali metal bicarbonates, and esters of polyols such as diacetin or triacetin.

It has now been found that certain diesters of succinic acid are very good gelling agents for alkali metal silicates, their efficiency being generally greater than that of the alkyl monoesters previously proposed, e.g. ethyl acetate, and than that of esters of polyols which still contain at least one free hydroxyl group, e.g. diacetin.

The liquid or gelled compositions of the present invention comprise an aqueous alkali metal silicate solution and, as gelling agent, a dialkyl succinate in which each alkyl radical contains 1 to 5 carbon atoms and/or the reaction products of the aforesaid compounds. Such a radical may, for example, be methyl, ethyl, propyl, butyl or isobutyl. Dimethyl succinate is preferred because of its good water solubility.

These diesters may be used by themselves or mixed with other gelling agents of a known type, such as, for example, ethyl acetate, ethylene glycol acetate, diacetin and triacetin.

The alkali metal silicate is generally a sodium, potassium or lithium silicate in which

the molar ratio $\text{SiO}_2:\text{M}_2\text{O}$ is 2.0:1 to 5.0:1, and preferably 3.4:1 to 5:1 (M being the alkali metal). They are normally used as aqueous solutions of 25 to 40% by weight solids content, such as for example sodium silicate solutions having a strength of 31 to 34 degrees Baume (at 20°C).

The relative proportions of succinic diester and alkali metal silicate may vary between wide limits. However, preferred amounts are 5 to 50 parts by weight (solids content) of dialkyl succinate for each 100 parts by weight of alkali metal silicate (solids content). Furthermore, when the dialkyl succinate is used conjointly with another gelling agent of known type, the respective proportions of the two gelling agents in the mixture may vary widely, for example from 100 to 60 parts (by weight) of succinate per 0 to 40 parts of the other gelling agent i.e. the second gelling agent may be present in an amount up to 40 parts by weight for each 100 parts by weight of the dialkyl succinate and second gelling agent.

A convenient way of expressing the relative amounts of the components in the compositions of the invention is to use the ratios:

$$a = \frac{\text{weight of gelling agent(s) in grams}}{\text{initial volume of silicate solution in cm}^3}$$

$$b = \frac{\text{volume of water added}}{\text{initial volume of silicate solution}}$$

Since, as already mentioned, silicates are ordinarily supplied as aqueous solutions, it is convenient to measure the amount of silicate used by the volume of the solution used, the "initial volume" in the above definitions. Any additional water may be added separately but is ordinarily added as the solvent in which the gelling agent(s) is dissolved. Changes in these ratios obviously affect the characteristics of the gels obtained. The characteristics which are

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generally regarded as most important are: the setting time of the gel; the compression resistance; the water sensitivity and the viscosity of the mixture of silicate and gelling agent(s); as well as the variation of the latter with respect to time. It is generally desirable for the setting time to be not less than 10 or 15 minutes nor greater than 1 hour, and a time of about 30 to 50 minutes is a good mean. The compression resistance is preferably between 10 and 30 kg/cm². Finally, the initial viscosity of the silicate/gelling agent mixture must be low, preferably less than 5 centipoises (at 20°C.), that is to say close to that of water. Furthermore it should increase with time sufficiently slowly to make it possible, during the consolidation of soils, to carry out the injection of the mixture and the cleaning of equipment before the gel has irreversibly set.

Bearing in mind these optimum properties, it may be stated that ratios "a" of between 0.02 and 0.15 and "b" of between 0.4 and 2 are generally very suitable, particularly when the diester used is dimethyl succinate. However, it has been observed that the three aforementioned characteristics of the gel assume their optimum values when "b" is from 0.6 to 1 (corresponding to slightly diluted silicate) whilst "a" is kept at from 0.04 to 0.12. Under these conditions, the setting time may vary between 5 and 125 minutes, the compression resistance is above 10 kg/cm² and the viscosities, which are of the order of 2 to 6 centipoises immediately after introducing the gelling agent or agents into the silicate, first increase slowly and then assume high values immediately before the formation of the gel.

The new compositions may be prepared by known techniques for making similar known compositions. It is preferred to introduce the aqueous solution of the gelling agent into the aqueous solution of the alkali metal silicate, kept at an ordinary temperature (of the order of 20°C.), over the course of 1 to 2 minutes.

The compositions so obtained are then ready

to be injected into soils which are to be consolidated and/or stabilized. They are easily handled and may be injected into particularly dense ground, as a result of their low initial viscosity which is close to that of water. They lead to the formation of gels which are extremely resistant to water, which have a compression resistance often greater than 15 kg/cm² and which change into a hard, coherent mass similar to cement.

The amounts of the mixtures of the invention to be used relative to the soil to be treated obviously vary according to the type of ground (whether clay, sand, etc.). However, it can be stated that generally from 10 to 60% of the gelling mixture based on the weight of soil, corresponding to 1 to 10% dry weight, should be injected.

The following Examples illustrate the invention.

EXAMPLE 1

A series of gels was prepared by mixing for immediate use, as explained above, aqueous sodium silicate solutions of 31° Baume, with 10% aqueous solutions of dimethyl succinate in various ratios "a" and "b" as defined above. The silicate used had a molar ratio SiO₂:Na₂O of 3.92.

The following properties of the mixtures obtained were then measured:

(a) the setting time T_p, this being the time necessary for the surface of a vessel filled with the gelling mixture no longer to show any deformation when inclined to the horizontal;

(b) the compression resistance R, measured as the resistance of the gel to the introduction of a needle of 1.18 cm² cross section, connected to a 100 kg tensometer collar, using gels which have aged for 48 hours, and kept under 5 mm. of water.

(c) the initial viscosity V, measured at a temperature of 20°C. with an EPPRECHT viscometer of the "Rheomat 15" type.

The results obtained are listed in Table I below.

TABLE I

Ratio b	Ratio a	Tp minutes	R (Kg/cm ²)
0.6	0.04	78	11.3
	0.05	45	17.9
	0.06	29	18.5
	0.08	12	20.8
	0.1	6	27.5
0.8	0.035	132	4.4
	0.05	67	10.9
	0.06	45	14.5
	0.075	24	15.0
	0.1	10	15.0
	0.12	6	15.0
1	0.04	125	2.4
	0.05	72	5.9
	0.075	30	11.6
	0.1	16	13.6
	0.12	8	13.6
	0.15	5	13.6
1.2	0.045	210	1.2
	0.05	86	3.8
	0.075	41	8.5
	0.1	21	10.8
	0.12	15	11.1
	0.14	11	11
1.5	0.05	178	1.5
	0.06	90	3
	0.075	56	5.2
	0.1	34	7.3
	0.12	25	8.0
	0.14	17	7.3
	0.16	14	7.3
	0.18	10	7.0

For the mixtures described in this Table, the initial viscosity V of the silicate solution containing the gelling agent varied between 1.5 and 5 centipoises. The viscosity of a composition having a molar ratio $\text{SiO}_2:\text{Na}_2\text{O}$ of 3.92, with "a" = 0.06 and "b" = 0.8, was 6 centipoises after 15 minutes and 10 centipoises at the end of 34 minutes, the setting time being about 45 minutes.

As may be seen from the Table, the results obtained are better when a ratio "b" of less than or equal to 1 is chosen. In that case the compression resistance of the gels attains values up to 28 kg/cm². Furthermore the gels obtained are very resistant to the action of water. Some of them can be kept entirely immersed in water for more than a month with a degree of degradation by weight of less than 1%.

EXAMPLE 2

In order to demonstrate the consolidating power of the new compositions on non-coherent materials, tests with dry Fontainebleau sand were carried out.

For this, test cylinders having a diameter of 37.5 mm. and a height of 75 mm. were filled with this sand. They were subjected to a gentle vibratory movement without tamping, and the sand was then impregnated by capillary action with gelling mixtures obtained according to Example 1. The amount of these varied between 1 and 10% of the weight of sand (expressed as solids content).

The test cylinders so prepared were then hermetically closed in order to keep the mixtures protected from air. Compression resistance was measured 24, 48 and 72 hours after the treatment. The results obtained are given in Table II below.

TABLE II

Value of ratios		Resistant (mean) kg/cm ² after		
a	b	24 hrs.	48 hrs.	72 hrs.
0.06	0.8	11.8	11.5	11.5
"	1	7.6	7	7.5
"	1.2	5.5	5.6	5.7
"	1.35	4.5	4.8	4.8
"	1.5	3.6	3.8	3.8

WHAT WE CLAIM IS:—

1. A liquid or gelled composition comprising an aqueous alkali metal silicate solution and, as gelling agent, a dialkyl succinate in which each alkyl radical contains 1 to 5 carbon atoms, and for the reaction products of the aforesaid compounds.

2. A composition according to claim 1 in which the dialkyl succinate is dimethyl succinate.

3. A composition according to claim 1 or 2 containing 5 to 50 parts by weight of the dialkyl succinate for each 100 parts by weight of the dry alkali metal silicate.

4. A composition according to any of claims 1 to 3 in which the molar ratio $\text{SiO}_2:\text{M}_2\text{O}$ in the alkali metal silicate (M being the alkali metal) is 2.0:1 to 5.0:1.

5. A composition according to any of claims 1 to 4 in which the alkali metal silicate is a sodium, lithium, or potassium silicate.

6. A composition according to any of claims 1 to 5 containing a second gelling agent in amount up to 40 parts by weight for each 100

parts by weight of the dialkyl succinate and second gelling agent.

7. A composition according to any of claims 1 to 6 in which the silicate is initially present as an aqueous solution of 25 to 40% by weight solids content.

8. A composition according to claim 7 in which the ratio

$$\frac{\text{weight of gelling agent (s) in grams}}{\text{initial volume of silicate solution in cm}^3}$$

is 0.02 to 0.15, and the ratio

$$\frac{\text{volume of water added}}{\text{initial volume of silicate solution}}$$

is 0.4 to 2.

9. A composition according to claim 8 in which the said ratios are 0.04 to 0.12 and 0.6 to 1.0 respectively.



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is 0.02 to 0.15, and the ratio

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is 0.4 to 2.

9. A composition according to claim 8 in which the said ratios are 0.04 to 0.12 and 0.6 to 1.0 respectively.



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10. A composition according to claim 1 substantially as described in the Examples.

1 to 10% by weight of the said composition (dry weight) based on the weight of the soil is introduced into the said soil.

11. Process for the consolidation and stabilization of soil which comprises introducing into said soil a liquid composition as claimed in any of claims 1 to 10.

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12. Process according to claim 11 in which

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