

PATENT SPECIFICATION

(11) 1 359 433

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(54) GELLING SILICATES

(71) We, RHONE-PROGIL, a French body corporate of 6 Rue Piccini, Paris 16eme, 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 compositions containing an alkali silicate gelled by certain dialkyl diesters.

In our British Patent Specification No. 1,159,400, we describe the use of alkyl diesters of succinic acid as gelling agent for alkali metal silicates and the use of the resulting mixture for the consolidation of soils and/or for rendering soils water-tight. We have now found, according to the present invention, that a mixture of alkyl diesters of succinic acid with alkyl diesters of the higher homologues of this acid, i.e. glutaric and adipic acids, also gels such silicates under analogous conditions. Accordingly the present invention provides a liquid or gelled composition comprising an aqueous alkali metal silicate solution and, as gelling agent, at least one dialkyl succinate and at least one dialkyl glutarate or adipate, in which each alkyl radical contains 1 to 5 carbon atoms.

The relative proportions of the different esters in the mixture is not critical. However, an excess of the diesters of glutaric and succinic acids relative to the diesters of adipic acid is preferred, because the most suitable setting times are obtained with compositions containing these esters in excess.

The mixture of diesters can result from the direct mixing of the diester or diesters of each acid prepared separately or from the esterification of mixtures of the said acids. The mixture of adipic, glutaric and succinic acids obtained as a residue in the mother liquors resulting from the crystallisation of adipic acid, forms a particularly valuable starting material. In effect, it is known that during the crystallisation of adipic acid, produced by oxidising cyclohexanone in the presence of nitric acid, large amounts of succinic, glutaric and adipic acids are found in the mother liquors. Because of their similar physical properties, these three

acids cannot be separated under economically viable conditions, and, most frequently, these are discharged into the sewage system. In addition to the pollution problem involved, the loss of products as valuable as these acids is unfortunate, especially because the concentration of the mixture of the three acids can be as high as 30% by weight in the mother liquors.

We have found, surprisingly, that this mixture, which hitherto has had very limited use, can be used in the formation of a perfectly suitable gelling reagent for alkali metal silicates.

According to a preferred method of esterifying the mixture of acids, the mother liquors are concentrated by heating in order to reduce the water content to of the order of 20% by weight. After having added an acid esterification catalyst, the alcohol corresponding to the desired diesters is gradually introduced, suitably keeping the temperature of the mixture at about 115°C. Under these conditions, the water-alcohol mixture which evaporates is distilled off in a conventional column, the water being removed and the alcohol being returned to the reaction. The amount of alcohol remaining in the mixture of diesters at the end of the reaction is low, and in all cases, as we have described in British Patent Specification No. 1,162,903, the presence of alcohol does not affect the final characteristics of the compositions based on alkali metal silicates gelled by alkyl esters.

Other methods of esterification, such as, for example, the action of an alkylene oxide, can also be used.

The diesters which are used according to the invention are alkyl diesters in which the alkyl radicals contain 1 to 5 carbon atoms, in particular methyl, ethyl, propyl, isopropyl, butyl and isobutyl radicals.

The gelling agent can consist of a mixture of diesters of succinic, glutaric and adipic acids which all possess the same alkyl groups or of a mixture of diesters which possess different alkyl groups.

The mixture of diesters can be used alone or as a mixture with other known gelling

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agents, such as ethyl acetate, ethyl glycol acetate, diacetin and triacetin.

In order to assist the dispersion of the diesters, it is possible to add an emulsifying agent which is compatible with the alkaline medium, such as the condensates of ethylene oxide with alkylphenols.

The alkali metal silicates which can be gelled by the esters can be sodium, potassium or lithium silicates or polysilicates, generally those in which the molar ratio $\text{SiO}_2/\text{M}_2\text{O}$ is 2.0:1 to 5.0:1, preferably 3.4:1 to 5:1 (M being an alkali metal). They are usually employed in the form of aqueous solutions, suitably of 25 to 40% by weight solids content, such as solutions of sodium silicates of strength 30 to 40 Baumé degrees (at 20°C).

The relative proportions of the mixture of alkyl diesters and alkali metal silicate can vary within wide limits. Preferably, however, 5 to 50 parts by weight of dry alkyl diester are used per 100 parts of dry alkali metal silicate.

Furthermore, when the alkyl diesters are used in conjunction with another gelling agent of known type, the respective proportions of the two gelling agents in the mixture can be very wide, for example 100 to 60 parts by weight of diesters per 0 to 40 parts by weight of the other reagent i.e. the second gelling agent can be used in an amount up to 40 parts by weight for each 100 parts by weight of the ester and the second gelling agent.

As was described in the Parent Specification, a convenient means of expressing the relative amounts of the constituents in the compositions involves using the ratios:

$$a = \frac{\text{weight of gelling agent (s)}}{\text{volume of silicate}}$$

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

It is interesting to note that the setting time of a composition of this invention, for a given pair (a, b), is related to the proportions of the diesters possessing different alkyl groups. Thus, for example, by varying the ratio by weight of methyl diesters/ethyl diesters, it is possible to adjust the setting time of a composition of this invention to a suitable value.

The compressive strength does not depend on the relative proportions of the diesters possessing different alkyl groups, but only on the values of the ratios a and b.

The compositions according to the invention can be prepared according to the conventional techniques for gelling alkali metal silicates. According to a particularly advantageous method of manufacture, the aqueous solution or dispersion of the gelling reagent is introduced, with stirring, over the course

of 1 to 2 minutes, into the aqueous solution of alkali metal silicate, kept at room temperature.

The compositions thus obtained are then ready to be introduced, for example, injected, into the soils which are intended to be rendered water-tight (stabilised) and/or consolidated. They are easy to handle and can be injected into ground which is rather impermeable, because of their low initial viscosity, which is close to that of water.

The amounts of the mixtures of this invention to be employed relative to the soil to be treated will obviously vary depending on the type of soil (clay, sand and similar granular and particulate materials). It can be stated, however, that, generally, between 10 to 60% of gelling material relative to the weight of soil, that is to say about 1 to 10% (dry weight) should be used.

The following Examples further illustrate the present invention. Examples 1 and 2 illustrate the preparation of the esters used in the compositions of this invention.

Example 1.

The mother liquors resulting from the manufacture of adipic acid from cyclohexanone are recovered to have available a mixture of methyl diesters of succinic, glutaric and adipic acids. These liquors have the following composition, by weight:

Succinic acid	6%	90
Glutaric acid	18%	
Adipic acid	6%	
Nitric acid	<0.5%	
Traces of metal	0.06%	
Water	about 70%	95

21 kg of a mixture having this composition are gradually introduced into a still. The mixture is kept at the boil for 18 hours (at 120°C) so as to evaporate a large part of the water. After 18 hours, the reaction medium has substantially the following composition, by weight:

Succinic acid	16%	
Glutaric acid	48%	
Adipic acid	16%	105
Water	20%	

50 g of concentrated sulphuric acid are then introduced, and then 4 kg of methanol are gradually added keeping the temperature at 115°C.

The water-alcohol mixture which evaporated is separated in a distillation column, the water being removed at the base and the alcohol vapours being condensed at the top and recycled to the reactor. The operation is continued for 12 hours, during which the acid number decreases and then becomes steady at about 5.

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7.600 kg of a liquid mixture which has the following composition, by weight, is then removed from the still:

5	Methyl succinate	19%	Ethyl adipate	23.3%	35
	Methyl glutarate	54.6%	Ethyl alcohol	1.7%	
	Methyl adipate	26.3%	Water	0.4%	
	Water	0.1%			

The mixture has an orange colour, and a density of 1.086 at 20°C and melts at -35°C.

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Example 2.

The mother liquors resulting from the manufacture of adipic acid from cyclohexanone, having the same composition as those of Example 1, are recovered in order to have available a mixture of ethyl esters of succinic, glutaric and adipic acids.

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28 kg of these mother liquors are introduced into a still and the mixture is kept at the boil for 20 hours. 80 g of concentrated sulphuric acid are then introduced, and then 8.960 kg of ethanol are gradually added, keeping the temperature at 115°C.

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The mixture of water and water-alcohol azeotrope which is evaporated is separated by distillation, the azeotrope being recycled after condensation. The operation is continued for 20 hours, at the end of which the acid number becomes steady at 15. 10.900 kg of a mixture which has the following composition by weight, are then removed:

25	Ethyl succinate	19.0%		
	Ethyl glutarate	55.6%		

The water-liquid mixture has an orange-yellow colour, and a density of 1.023 and melts at -42°C.

The following Examples illustrate how the present invention can be put into practice.

A complete series of gels was prepared by mixing, at the time of use, according to the technique described in the Parent Specification, aqueous solutions of sodium silicates with aqueous solutions or dispersions containing varying amounts of gelling agent. The final compositions are given in terms of the ratios a and b defined above.

The principal characteristics of the mixtures obtained were then measured, i.e.

1) The setting time which is the time necessary for the surface of a container, filled with the mixture to be gelled and inclined to the horizontal, no longer to show any deformation.

2) The viscosity measured at a temperature of 20°C with a "Rhéomat 15" Epprecht viscometer.

The results obtained are given in Tables 1 and 2 below.

A series, A, of compositions with a gelling agent defined in Example 1, and a series, B, of compositions with a 50/50 mixture by weight of the gelling agents defined in Examples 1 and 2, were prepared with an aqueous solution of sodium silicate of strength 31° Baumé, the molar ratio SiO₂/Na₂O being equal to 3.84.

TABLE 1

Value of the ratios		Setting time		Viscosity in centipoise
a	b	Series A minutes	Series B minutes	
0.06	0.8	45	81	5.7
	1	63	101	5.6
	1.2	84	127	5.4
	1.35	110	170	5.2
	1.50	148	241	5.0
0.08	0.8	27	60	5.7
	1	36	64	5.6
	1.2	48	71	5.4
	1.35	58	81	5.2
	1.50	72	97	5.0
0.1	0.8	20	53	5.7
	1	24	54	5.6
	1.2	31	57	5.4
	1.35	36	60	5.2
	1.50	45	67	5.0

Two series of compositions with the same strength 39° Baumé, the molar ratio 5 gelling agents as above were prepared with $\text{SiO}_2/\text{Na}_2\text{O}$ being equal to 3.34. an aqueous solution of sodium silicate of

TABLE 2

Value of the ratios		Setting time		Viscosity in centipoise
a	b	Series A minutes	Series B minutes	
0.06	0.8	87	162	7.3
	1	128	204	6.7
	1.2	172	246	6.3
	1.35	233	311	6.0
	1.50	325	411	5.8
0.08	0.8	50	112	7.3
	1	64	126	6.7
	1.2	83	144	6.3
	1.35	101	163	6.0
	1.50	126	190	5.8
1	0.8	37	92	7.3
	1	43	97	6.7
	1.2	50	107	6.3
	1.35	56	115	6.0
	1.50	68	131	5.8

An application of the compositions according to the invention in the consolidation of soils will now be given.

- 5 A cylindrical mould, of internal diameter 40 mm and of length 1,500 mm, is filled with dry Fontainebleau sand. After compressing the sand, a composition according to the invention, which is prepared with an aqueous solution of sodium silicate and a mixture of methyl and/or ethyl diesters at various concentrations, is injected through the base of the mould.

- 10 After the composition has set solid, the mould is cut up into cylindrical test pieces, 80 mm in height, which are stored in a sealed chamber at 20°C for 7 days.

The test pieces of agglomerated sand are then removed from the mould and subjected to a simple compression crushing experiment by means of a press, the speed of movement of which is adjusted to 20 mm/minute. The force necessary to rupture the test pieces is noted and it is related to the surface area of the base, which gives the compressive strengths, expressed in kg/cm².

Test pieces as defined above were prepared by injecting into the sand compositions identical to those studied in Tables 1 and 2.

The values of the compressive strengths of the test pieces thus produced are given in Table 3.

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TABLE 3

Value of the ratios		Aqueous solution of Na silicate, of strength 31° Baumé, $\text{SiO}_2/\text{Na}_2\text{O}=3.84$	Aqueous solution of Na silicate, of strength 39° Baumé, $\text{SiO}_2/\text{sNa}_2\text{O}=3.34$
a	b	S in kg/cm ²	S in kg/cm ²
0.06	0.8	14.04	14.66
	1	11.19	11.00
	1.2	9.15	8.47
	1.35	7.83	6.38
	1.50	6.56	4.19
0.08	0.8	14.45	20.06
	1	11.35	14.98
	1.2	9.17	11.61
	1.35	7.88	9.67
	1.50	6.76	7.93
0.1	0.8	14.34	23.18
	1	10.96	17.22
	1.2	8.56	13.17
	1.35	7.14	11.04
	1.50	6.11	9.38

It can be seen that the compressive strengths obtained are markedly higher than those given in the Parent Specification. This is believed to be partly due to the fact that the test pieces are produced here by injection of the composition according to the invention and not by impregnation by capillary action.

The technical value of the gelling agent used in the compositions of this invention in the consolidation of soils rests on the fact that the setting time is longer than that of the agent described in the main patent, which makes it possible to inject compositions which have greater proportions of gelling agent and silicate, and this gives rise to very much better mechanical strengths because of the increase in the concentration of the injected products.

WHAT WE CLAIM IS:—

1. A liquid or gelled composition comprising an aqueous alkali metal silicate solution, and as gelling agent, a dialkyl succinate and at least one dialkyl glutarate or adipate, in which each alkyl radical contains 1 to 5 carbon atoms.

2. A composition according to Claim 1, in which the dialkyl esters are obtained by esterifying the mixture of succinic, glutaric and adipic acids, obtained as mother liquor from the crystallisation of adipic acid manufactured by oxidising cyclohexanone.

3. A composition according to Claim 1 or 2, which also contains a compatible emulsifying agent.

4. A composition according to any one 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 5:1.

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

6. A composition according to any one of Claims 1 to 5 containing 5 to 50 parts by weight of dry ester for each 100 parts by weight of the dry alkali metal silicate.

7. A composition according to any one of the preceding Claims containing a second gelling agent in an amount up to 40 parts by weight for each 100 parts by weight of the ester and second gelling agent.



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TABLE 3

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	1	11.19	11.00
	1.2	9.15	8.47
	1.35	7.83	6.38
	1.50	6.56	4.19
0.08	0.8	14.45	20.06
	1	11.35	14.98
	1.2	9.17	11.61
	1.35	7.88	9.67
	1.50	6.76	7.93
0.1	0.8	14.34	23.18
	1	10.96	17.22
	1.2	8.56	13.17
	1.35	7.14	11.04
	1.50	6.11	9.38

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The technical value of the gelling agent used in the compositions of this invention in the consolidation of soils rests on the fact that the setting time is longer than that of the agent described in the main patent, which makes it possible to inject compositions which have greater proportions of gelling agent and silicate, and this gives rise to very much better mechanical strengths because of the increase in the concentration of the injected products.

WHAT WE CLAIM IS:—

1. A liquid or gelled composition comprising an aqueous alkali metal silicate solution, and as gelling agent, a dialkyl succinate and at least one dialkyl glutarate or adipate, in which each alkyl radical contains 1 to 5 carbon atoms.

2. A composition according to Claim 1, in which the dialkyl esters are obtained by esterifying the mixture of succinic, glutaric and adipic acids, obtained as mother liquor from the crystallisation of adipic acid manufactured by oxidising cyclohexanone.

3. A composition according to Claim 1 or 2, which also contains a compatible emulsifying agent.

4. A composition according to any one 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 5:1.

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

6. A composition according to any one of Claims 1 to 5 containing 5 to 50 parts by weight of dry ester for each 100 parts by weight of the dry alkali metal silicate.

7. A composition according to any one of the preceding Claims containing a second gelling agent in an amount up to 40 parts by weight for each 100 parts by weight of the ester and second gelling agent.

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8. A composition according to Claim 1 substantially as hereinbefore described.

9. A composition according to Claim 1 substantially as described in any one of the

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10. Process for the consolidation and stabilisation of soil (as hereinbefore defined) which comprises introducing into said soil a liquid composition as claimed in any one of

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11. Process according to Claim 10 in which 1 to 10% by weight of the said composition (dry weight) based on the weight of the soil is incorporated into the said soil.

12. Process according to Claim 10 substantially as hereinbefore described.

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