



PROCESS FOR THE PREPARATION OF PUMPABLE CLAYEY AQUEOUS MIXTURES

The present invention relates to a process which makes it possible to improve the use and the handleability of clay-based aqueous mixtures and also relates to the mixtures thus transformed.

5 In general, clays consist of aluminium silicates, iron silicates and/or magnesium silicates which are hydrated and may additionally contain other ions including more particularly the sodium, calcium and potassium ions. These silicates are commonly called
10 mineral clays. The main groups of mineral clays are kaolinites, smectites, illites, chlorites and hormites.

As a result of their abundance on earth and of their various properties which are closely linked with their mineral compositions, clays are materials
15 which have very varied uses and are therefore extensively exploited.

Subsoil extraction of clay, either with a view to its exploitation or in the context of construction work of the type of excavation of
20 underground galleries, usually requires its conversion into an aqueous slurry by incorporating water. This aqueous slurry or aqueous mud is then removed from the underground cavities by virtue of pumps. The percentage of solid particles in this aqueous clay slurry is
25 normally between 30 and 40 %, but it may also exceed 70 %. In this latter case it becomes difficult to obtain a paste which is sufficiently fluid to be pumpable.

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To overcome this disadvantage it has been recommended to add to these aqueous clay slurries a chemical dispersing agent the purpose of which is to bring them into a more fluid and more easily pumped form. The most widely employed dispersing agents are water-soluble polyphosphate, silicate or polyacrylate salts. However, the use of these products is not entirely satisfactory.

It has now been found - and this is what forms the subject-matter of the present invention - that it is possible advantageously to replace the dispersing agent as described above with a surface-active composition including a dispersing agent and a wetting agent.

More particularly the present invention provides a process for improving the use and the handleability of clay-based aqueous mixtures, characterized in that it consists in adding to the said aqueous clay mixture a surface-active composition consisting of:

- 10 to 90 weight %, preferably from 25 to 75 weight %, of at least one carbohydrate ester and/or a polyol ester

- and from 90 to 10 weight %, preferably from 75 to 25 weight %, of an alkoxyated triglyceride and/or at least one alkoxyated fatty acid.

It has been found, surprisingly, that when

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compared with the conventional process, only the process according to the invention makes it possible to provide within a very short period clayey aqueous mixtures endowed with plastic properties such that their pumpability is thereby very markedly improved.

Moreover, it should be noted that the process according to the invention is completely safe with regard to the environment, since the surface-active composition employed according to the invention is completely biodegradable.

"Plasticity" is intended to refer to the ability of the moistened clay to deform on the application of a light pressure and to maintain this deformation after this pressure has disappeared.

The term "clay" denotes, according to the present invention and in accordance with Grim's definition (Clay Mineralogy 1st ed. McGraw-Hill, N.Y. 1953, p.384), any argillaceous material of natural origin, finely granulated, and more particularly clays and schists.

As example of polyol esters it is possible to mention:

- esters of C_8-C_{22} , preferably $C_{10}-C_{20}$, fatty acids and of sorbitan, such as sorbitan laurate, sorbitan oleate etc.,

- esters of C_8-C_{22} , preferably $C_{10}-C_{20}$, fatty acids and of glycerol, such as food-grade monoglycerides and diglycerides,

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- polyglycerol polyricinoleate etc.

Insofar as carbohydrate esters are concerned it is possible to mention more particularly esterified or transesterified sugars such as sugar glycerides and sugar esters. Sugar glycerides are preferably involved.

The term "sugar glyceride" refers generally to the mixture of products obtained by the transesterification of sucrose and of natural or synthetic triglycerides. This mixture contains sucrose monoglycerides, diglycerides, unchanged triglycerides (in small quantities), monoesters and diesters.

As for the term "triglyceride", this refers to one or more triglycerides of saturated or unsaturated aliphatic fatty acids containing at least 12 carbon atoms and preferably 14 to 20 carbon atoms. It is obviously possible to start with a synthetic triglyceride obtained by the reaction of glycerol and fatty acid but, for economic reasons, it is more advantageous to rely on natural triglycerides, which are mixtures. Examples of natural triglycerides which may be mentioned are lard, tallow, groundnut oil, butter oil, cottonseed oil, linseed oil, coconut oil, olive oil, palm oil, grapeseed oil, fish oil, soya oil, castor oil, copra oil and rapeseed oil.

Sugar glycerides from lard, palm, copra, tallow and rapeseed oil are preferably employed. They are in a liquid form or in the form of pastes of varying consistency which differ commercially in their

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melting point.

A method of preparation which is particularly suited for these sugar glycerides is described in Patent Application FR 2 463 512.

5 With regard to the second constituent of the surface-active composition employed according to the invention, this may be:

- alkoxyated $C_{12}-C_{22}$ triglycerides containing approximately from 1 to 60 oxyalkylene units, such as
10 ethoxylated oils of vegetable or animal origin, such as ethoxylated castor, fish, copra, soya, palm, tallow, butter and similar oils, or

- an alkoxyated C_8-C_{22} , preferably $C_{10}-C_{20}$, fatty acid containing approximately from 1 to 60
15 oxyalkylene units, such as, for example, ethoxylated oleic or stearic acid.

The term "alkoxyated triglyceride" in the present invention relates both to the products obtained by alkoxylation of a triglyceride with an alkylene
20 oxide and those obtained by transesterification of a triglyceride with a polyalkylene glycol.

Similarly, "alkoxyated fatty acid" covers both the products obtained by alkoxylation of a fatty acid with an alkylene oxide and those obtained by
25 esterification of a fatty acid with a polyalkylene glycol.

The preferred surface agents forming the second constituent of the surface-active composition

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are ethoxylated oils and, in particular, mixtures thereof.

The surface-active composition of the invention can be prepared by mixing its different constituents in the liquid state. In the preferred case where one of the constituents is a sugar glyceride which is solid at ambient temperature, this is melted at about 60 to 80°C before the other components are incorporated therein in the liquid state.

According to the invention a mixture of sugar glyceride and of at least one polyethylene glycol ester of fatty acids is preferably employed as surface-active composition.

The clay-based aqueous mixture preferably includes at least 30 % and preferably more than 70 % by weight of solid particles.

The surface-active composition according to the invention may be introduced either directly into the clay-based aqueous mixture or may be incorporated as a mixture with water into the clay.

The quantity of surface-active composition introduced into the clay-based aqueous mixture may vary within wide limits.

However, the introduction of this composition is performed more particularly in a quantity of the order of 0.1 to 10 % and preferably of the order of 0.5 % to 8 % by weight relative to the weight of the clay-based aqueous mixture.

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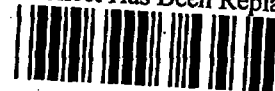
The process according to the invention applies successfully to the extraction of clayey materials from the subsoil and is, of course, equally advantageous for the subsequent conversion of aqueous clay mixtures into diverse materials such as, for example, bricks or ceramics.

In effect, from the viewpoint of use, kaolinites are employed for paper coating and for the manufacture of ceramics, and illites and kaolinites are employed as mixtures for the manufacture of tiles and bricks. Montmorillonites and attapulgites are involved as absorbents in numerous purification processes. Montmorillonites are also important constituents of drilling muds. Finally, the plasticity of kaolins and montmorillonites is also exploited for the manufacture of foundry moulds. The process according to the present invention is consequently capable of being used efficaciously for one or other of the abovementioned applications.

The present invention also relates to the clayey aqueous mixtures incorporating the surface-active composition described according to the invention, as well as to the various materials originating from these clayey aqueous mixtures, provided that they also contain the said surface-active composition.

The examples introduced below are by way of illustration.

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They were carried out by incorporating different surface-active systems into water/clay mixtures. The plasticity of the resulting mixtures was measured with the aid of a Brabender device (paddle mixer); this measurement consists in recording the resistance offered by a paste to the mixing; the more a paste offers a high resistance to the mixing (high Brabender viscosity), the more it is viscous and/or nonhomogeneous; the Brabender viscosity is zero when the paste is very fluid and homogeneous.

Example 1

An aqueous mixture is prepared from the following constituents:

- 5 g of water
- 20 g of clay
- 2 g of Celynol X8066 (marketed by Rhône-Poulenc), consisting of
 - 1/3 of ethoxylated castor oil
 - 1/3 of ethoxylated copra oil
 - 1/3 of sugar rapeseed glyceride.

The appearance of this composition is shown in Table I.

Example 2

An aqueous mixture is prepared from the following constituents:

- 20 g of water
- 20 g of clay
- 2 g of Celynol X8066 (marketed by

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Rhône-Poulenc), consisting of

1/3 of ethoxylated castor oil

1/3 of ethoxylated copra oil

1/3 of sugar rapeseed glyceride.

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The appearance of this composition is shown in Table I.

By way of comparison, compositions similar to those of Examples 1 and 2 were produced by replacing Celynol X8066 with the same weight of one of the

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following surfactants or surfactant mixture:

- T51 potassium silicate from Rhône-Poulenc

- Geropon HB (Na polyacrylate marketed by Rhône-Poulenc)

- Soprophor BC 10 (nonylphenol marketed by Rhône-Poulenc)

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- a 50/50 Soprophor BC 10/T51 potassium silicate mixture.

The appearances of these compositions are shown in Table I.

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TABLE I

Surfactant	Appearance with 5 g of water	Appearance with 20 g of water
TS1 silicate	mixing difficult liquid and many agglomerates	liquid sedimentation of the agglomerates
Geropon BB	more or less liquid paste agglomerates	fluid paste many agglomerates
Soprophor BC 10	dry, foamy mixture agglomerates	fairly homogeneous fine foam flocculation after 24 h
Soprophor BC 10/ TS1 silicate	fairly homogeneous paste fine agglomerates	fluid paste a few agglomerates flocculation after 24 h
Calymol X8066	pumpable homogeneous paste	pumpable homogeneous paste

Example 3

An aqueous mixture is prepared from the following constituents:

- 400 g of Flanders clay
- 100 g of water
- one of the surfactants which appear in Table II,

in a % relative to the clay + water mixture which appears in Table II

The Brabender plasticity of the mixtures obtained appears in Table II

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TABLE II

	Surfactant	Concentration	Brabender plasticity
	Rhodacal WP	0.5 %	650
	Geropon HB	0.5 %	heterogeneous mixture
5	Soprophor BO 327	0.5 %	300 ..
	Rhodacal WP/ T51 silicone	0.6 % (0.3/0.3)	heterogeneous mixture
	Rhodacal WP/ Geropon HB	1.3 % (1/0.3)	220
10	Soprophor BO 327 /T51 silicone	2 % - (1/1)	300
	Celynol X8066	1 %	0 -
	Celynol X8066	0.5 %	0

- Rhodacal WP (diisopropylnaphthalenesulphonate
15 marketed by Rhône-Poulenc)
- Soprophor BO 327 (alkoxylated fatty alcohol marketed
by Rhône-Poulenc)

Only the use of Celynol X8066 therefore makes
it possible to produce a zero plasticity and therefore
20 a good handleability of the clayey mixture which is
treated.

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Example 4

In this example the period for reaching plasticity equilibrium was measured, that is to say the time needed to obtain a mixture; a short time reflects the ease with which water is incorporated into the clay.

The mixture of Example 3 according to the invention (with 0.5 % of Celynol X8066) was compared with the mixture containing 0.5 % of Rhodacal WP and with a water/clay control mixture.

The results obtained appear in Table III.

Table III

Mixture	Brabender plasticity	Time to reach equilibrium (seconds)
Water/clay	1000	
Water/clay/ Rhodacal WP	650	120
Water/clay/ Celynol X8066	0	60

The best result obtained is indeed that of the mixture of the invention.



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CLAIMS

1. Process for improving the use and the handleability of clay-based aqueous mixtures, which comprises adding to a clay-based aqueous mixture a surface-active composition comprising:

- from 10 to 90 weight % of at least one carbohydrate ester and/or polyol ester, and
- from 90 to 10 weight %, of at least one alkoxyated triglyceride and/or alkoxyated fatty acid.

2. Process according to claim 1, in which from 25 to 75 weight % of at least one carbohydrate ester and/or polyol ester, and

from 75 to 25 weight % of at least one alkoxyated triglyceride and/or alkoxyated fatty acid is added.

3. Process according to claim 1 or 2, in which the polyol ester is an ester of at least one C_8-C_{22} fatty acid and of sorbitan, an ester of at least one C_8-C_{22} fatty acid and of glycerol or polyglycerol polyricinoleate.

4. Process according to claim 3, in which the polyol ester is an ester of at least one $C_{10}-C_{20}$ fatty acid and of sorbitan or an ester of at least one $C_{10}-C_{20}$ fatty acid and of glycerol.

5. Process according to any one of claims 1 to 4, in which the carbohydrate ester is a sugar glyceride or a sugar ester.

6. Process according to any one of the

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preceding claims, in which the alkoxyated triglyceride is an alkoxyated $C_{12}-C_{22}$ triglyceride containing from 1 to 60 oxyalkylene units.

7. Process according to any one of the preceding claims, in which the alkoxyated fatty acid is an alkoxyated C_8-C_{22} fatty acid containing from 1 to 60 oxyalkylene units.

8. Process according to claim 7 in which the fatty acid contains from 10 to 20 carbon atoms.

9. Process according to any one of the preceding claims, in which the clay-based aqueous mixture includes at least 30 % by weight of solid particles.

10. Process according to claim 9, in which the clay-based aqueous mixture includes at least 70% by weight of solid particles.

11. Process according to any one of the preceding claims in which the quantity of surface-active composition introduced is from 0.1 to 10 % by weight relative to the weight of the clay-based aqueous mixture.

12. Process according to claim 11, in which the quantity of surface active composition introduced is from 0.5 to 8 % by weight relative to the weight of the clay-based aqueous mixture.

13. Process according to any one of the preceding claims substantially as described in Example 1, 2 or 3.

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14. Process for extracting clayey materials from subsoil which comprises adding water and a surface-active composition as defined in any one of claims 1 to 13.

15. Clayey aqueous mixture which comprises:
- 100 parts by weight of a clay-based aqueous mixture containing at least 30 % by weight of solid particles, and

- from 0.1 to 10 % by weight relative to the weight of the clay-based aqueous mixture of a surface-active composition which comprises:

from 10 to 90 weight %, of at least one carbohydrate ester and/or polyol ester,

and from 90 to 10 weight %, of at least one alkoxyated triglyceride and/or alkoxyated fatty acid.

16. Clayey aqueous mixture according to claim 15, which comprises at least 70% by weight of solid particles.

17. Clayey aqueous mixture according to claim 15 or 16 which comprises from 0.5 to 8 parts by weight of a surface-active composition.

18. Clayey aqueous mixture according to any one of claims 15 to 17 which comprises from 25 to 75 weight % of at least one carbohydrate ester and/or polyol ester,

and from 75 to 25 weight % of at least one alkoxyated triglyceride and/or alkoxyated fatty acid.

19. Clayey aqueous mixture according to any

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one claims 15 to 18, in which the polyol ester is an ester of at least one C_8-C_{22} fatty acid and of sorbitan, an ester of at least one C_8-C_{22} fatty acid and of glycerol or polyglycerol polyricinoleate.

20. Clayey aqueous mixture according to claim 19 in which the polyol ester is an ester of at least one $C_{10}-C_{20}$ fatty acid and of sorbitan or an ester of at least one $C_{10}-C_{20}$ fatty acid and of glycerol.

21. Clayey aqueous mixture according to any one of claims 15 or 20, in which the carbohydrate ester is a sugar glyceride or a sugar ester.

22. Clayey aqueous mixture according to any one of claims 15 to 21, in which the alkoxylated triglyceride is an alkoxylated $C_{12}-C_{22}$ triglyceride containing from 1 to 60 oxyalkylene units.

23. Clayey aqueous mixture according to any one of claims 15 to 22, in which the alkoxylated fatty acid is an alkoxylated C_8-C_{22} fatty acid containing from 1 to 60 oxyalkylene units.

24. Clayey aqueous mixture according to claim 23 in which the alkoxylated fatty acid is an alkoxylated $C_{10}-C_{20}$ fatty acid.

25. Clayey aqueous mixture according to any one of claims 15 to 24 substantially as described in Example 1, 2 or 3.

26. Clayey aqueous mixture whenever improved by a process as claimed in any one claims 1 to 13.

27. Article derived from a clayey aqueous mixture as claimed in any one of claims 15 to 25.

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