EP 1 184 406 A2 discloses a process for preparing polymer powders, preferably based for on styrene-butadiene copolymers, via spray drying an aqueous dispersion of a film-forming polymer, which may be styrene-butadiene copolymers, a drying assistant selected from salts of oligomeric arylsulfonic acid-formaldehyde condensates and one anionic emulsifiers. The anionic emulsifier must be present in the aqueous polymer dispersion, before spray drying. A non-ionic emulsifier may also be used, but only in addition to the anionic emulsifier already mentioned. The polymer powders disclosed in EP 1 184 406 A2 are suitable as cobinders in binding mineral building materials and their formulations. Cementing of oilwells is not mentioned.

The demands on hydraulic binders to be used in the civil construction industry and those to be used in the oil industry for cementing oilwells are very different. In civil construction applications a fast gel strength development and a high adhesive strength often is necessary. By the way of example, tiles should adhere to the wall and remain in place even if the tile adhesive has not yet been set. By contrast, hydraulic cement compositions for oilwell cementing should have a low viscosity for a significant time after mixing so that they are pumpable and can be properly placed into the annulus between the casing and the wall of the wellbore before the hydraulic cement composition sets. A rectangular setting behavior is highly desirable, i.e. that the gel strength of the hydraulic cement composition for a certain time, for example a few hours, does not increase much and is pumpable. However, as soon as the cement slurry is placed in the annulus, fast gel build-up and short transition time from a liquid cement slurry to a cement slurry which can’t be penetrated by intruding gas from the formation is highly desirable.

It was the object of the present disclosure, to provide improved water-dispersible polymer powders for use as anti-fluid-loss additives in well cementing, in particular oilwell cementing which simultaneously improve the setting behavior of the hydraulic cementing composition.

In an aspect, there is provided a water-dispersible polymer powder composition (P) for use as additive in cementing in subterranean formations comprising at least

- 50 to 98.5 wt.-% of particles of a styrene-butadiene polymer (A),
- 1 to 20 wt.-% of at least one water-soluble polymer (B), selected from the group of phenol sulfonic acid – formaldehyde condensates, naphthalene sulfonic acid – formaldehyde condensates, melamine-formaldehyde condensates, and formaldehyde-acetone-sulfite condensates,

- 0.5 to 10 wt.-% of at least one non-ionic emulsifier (C),

wherein the amounts relate to the total of all components of the composition (P), and

wherein the styrene-butadiene polymer particles are at least partly covered by and/or embedded in a composition (X) comprising at least the water-soluble polymer (B).

In another aspect, there is also provided a process for making a water-dispersible polymer powder composition (P) as defined above, comprising spray-drying an aqueous polymer dispersion in the presence of a spray-drying aid, wherein process comprises at least the following process steps:

(1) providing an aqueous dispersion for spray-drying (S) by mixing at least

- an aqueous polymer dispersion comprising particles of a styrene-butadiene polymer (A), and
- a spray-drying aid which comprises at least one water-soluble polymer (B), selected from the group of phenol sulfonic acid – formaldehyde condensates, naphthalene sulfonic acid – formaldehyde condensates, melamine-formaldehyde condensates, and formaldehyde-acetone-sulfite condensates, and

(2) spray-drying the resultant aqueous dispersion (S),

wherein at least one non-ionic emulsifier (C) is added to the aqueous dispersion for spray-drying (S), and/or mixed with the spray-dried product after spray drying.

In another asepct, there is provided the use of a water-dispersible polymer powder composition (P) comprising at least

- 50 to 98.5 wt.-% of particles of a styrene-butadiene polymer (A),
- 1 to 20 wt.-% of at least one water-soluble polymer (B), selected from the group of phenol sulfonic aid – formaldehyde condensates, naphthalene sulfonic acid – formaldehyde condensates, melamine-formaldehyde condensates, formaldehyde-acetone-sulfite condensates, and copolymers comprising at least ethylenically unsaturated monomers comprising sulfonic acid groups and ethylenically unsaturated monomers comprising carboxylic acid groups,

wherein the amounts relate to the total of all components of the composition (P), and

wherein the styrene-butadiene polymer particles are at least partle covered by and/or embedded in a composition (X) comprising at least the water-soluble polymer (B),

for cementing in subterranean formations penetrated by at least a well bore comprising at least the following steps:

(a) preparing an aqueous cement slurry by mixing at least a hydraulic cement, the water-dispersible polymer powder composition (P), and sufficient water to form a pumpable slurry;

(b) placing said aqueous cement slurry through a well bore to a zone to be cemented, and

(c) allowing said aqueous cement slurry to set

wherein additionally 0.5 to 10 wt.-% of at least one non-ionic emulsifier (C) are comprised in the water-dispersible polymer powder composition (P) or added to the aqueous cement slurry.

In another aspect, there is provided a dry cement composition comprising at least

- a hydraulic cement, and
- a water-dispersible polymer powder composition (P) as defined above.

Accordingly, in a first embodiment of the invention a water-dispersible polymer powder composition (P) for use as additive in cementing in subterranean formations has been found, comprising at least

- 50 to 98.5 wt.-% of particles of a styrene-butadiene polymer (A),
- 1 to 20 wt.-% of at least one water-soluble polymer (B), selected from the group of phenol sulfonic acid–formaldehyde condensates, naphthalene sulfonic acid–formaldehyde condensates, melamine-formaldehyde condensates, formaldehyde-acetone-sulfite condensates, and copolymers comprising at least ethylenically unsaturated monomers comprising sulfonic

**Claims:**

1. Water-dispersible polymer powder composition (P) for use as additive in cementing in subterranean formations comprising at least

   - 50 to 98.5 wt.-% of particles of a styrene-butadiene polymer (A),
   - 1 to 20 wt.-% of at least one water-soluble polymer (B), selected from the group of phenol sulfonic acid – formaldehyde condensates, naphthalene sulfonic acid – formaldehyde condensates, melamine-formaldehyde condensates, and formaldehyde-acetone-sulfite condensates,
   - 0.5 to 10 wt.-% of at least one non-ionic emulsifier (C),

   wherein the amounts relate to the total of all components of the composition (P), and

   wherein the styrene-butadiene polymer particles are at least partly covered by and/or embedded in a composition (X) comprising at least the water-soluble polymer (B).

2. Water-dispersible polymer powder composition (P) according to claim 1, wherein the composition (X) comprises the non-ionic emulsifier(s) (C).

3. Water-dispersible polymer powder composition (P) according to claim 1, wherein the composition (P) is a mixture of the non-ionic emulsifier(s) (C) and styrene-butadiene polymer particles (A) which are at least partly covered by and/or embedded in a composition (X).

4. Water-dispersible polymer powder composition (P) according to any of claims 1 to 3, wherein the composition (P) comprises additionally up to 30 wt.-% of an anti-blocking agent(s) (D), wherein the amount relates to the total of all components of the composition (P).

5. Water-dispersible polymer powder composition (P) according to any of claims 1 to 4, wherein the non-ionic emulsifier (C) has the general formula

$$R^1\text{-}O\text{-}(CH_2\text{-}CHR^2O)_nH,$$

wherein $R^1$ is a linear or branched aliphatic hydrocarbon moiety comprising 12 to 20 carbon atoms, $R^2$ is selected from the group of H, methyl and ethyl, wherein at least 50% of all $R^2$ groups are H, and n is from 15 to 50.

6. Water-dispersible polymer powder composition (P) according to any of claims 1 to 5, wherein the water-soluble polymers comprise at least phenol sulfonic acid–formaldehyde condensates.

7. Water-dispersible polymer powder composition (P) according to any of claims 4 to 6, comprising,

- 60 to 96 wt.-% of the particles of the styrene-butadiene polymer (A),
- 1 to 15 wt.-% of at the water-soluble polymer(s) (B),
- 1 to 7 wt.-% of non-ionic emulsifier(s) (C), and
- 1 to 20 wt. % of anti-blocking agent(s) (D),

wherein the amounts relate to the total of all components of the composition (P).

8. Water-dispersible polymer powder composition (P) according to any of claims 4 to 6, comprising,

- 70 to 90 wt.-% of the particles of the styrene-butadiene polymer (A),
- 3 to 12 wt.-% of at the water-soluble polymer(s) (B), comprising at least a phenol sulfonic acid – formaldehyde condensate,
- 1 to 5 wt.-% of non-ionic emulsifier(s) (C), having the formula $R^1$-O-($CH_2$-$CHR^2$)$_n$H, wherein $R^1$, $R^2$, and n have the meaning as defined, and
- 5 to 15 wt. % of anti-blocking agent(s) (D),

wherein the amounts relate to the total of all components of the composition (P).

9. Process for making a water-dispersible polymer powder composition (P) according to claim 1, comprising spray-drying an aqueous polymer dispersion in the presence of a spray-drying aid, wherein process comprises at least the following process steps:

(1) providing an aqueous dispersion for spray-drying (S) by mixing at least

- an aqueous polymer dispersion comprising particles of a styrene-butadiene polymer (A), and
- a spray-drying aid which comprises at least one water-soluble polymer (B), selected from the group of phenol sulfonic acid – formaldehyde condensates, naphthalene sulfonic acid – formaldehyde condensates, melamine-formaldehyde condensates, and formaldehyde-acetone-sulfite condensates, and

(2) spray-drying the resultant aqueous dispersion (S),

wherein at least one non-ionic emulsifier (C) is added to the aqueous dispersion for spray-drying (S), and/or mixed with the spray-dried product after spray drying.

10. Process according to claim 9, wherein the non-ionic emulsifier (C) is added to the aqueous dispersion for spray-drying (S).

11. Process according to claim 9, wherein the non-ionic emulsifier (C) is mixed with the spray-dried product after spray drying.

12. Process according to any of claims 9 to 11, wherein at least one anti-blocking agent (D) is added during and/or after spay-drying, wherein the amount of the anti-blocking agent(s) is up to 30 wt.-%, relating to the total of all components of the composition (P).

13. Process according to any of claims 9 to 12, wherein the non-ionic emulsifier (C) has the general formula

$$R^1\text{-}O\text{-}(CH_2\text{-}CHR^2O)_nH,$$

wherein $R^1$ is a linear or branched aliphatic hydrocarbon moiety comprising 12 to 20 carbon atoms, $R^2$ is selected from the group of H, methyl and ethyl, wherein at least 50% of all $R^2$ groups are H, and n is from 15 to 50.

14. Process according to any of claims 9 to 13, wherein the water-soluble polymers comprise at least phenol sulfonic acid – formaldehyde condensates.

15. Use of a water-dispersible polymer powder composition (P) comprising at least

- 50 to 98.5 wt.-% of particles of a styrene-butadiene polymer (A),

- 1 to 20 wt.-% of at least one water-soluble polymer (B), selected from the group of phenol sulfonic aid – formaldehyde condensates, naphthalene sulfonic acid – formaldehyde condensates, melamine-formaldehyde condensates, formaldehyde-acetone-sulfite condensates, and copolymers comprising at least ethylenically unsaturated monomers comprising sulfonic acid groups and ethylenically unsaturated monomers comprising carboxylic acid groups,

wherein the amounts relate to the total of all components of the composition (P), and

wherein the styrene-butadiene polymer particles are at least partle covered by and/or embedded in a composition (X) comprising at least the water-soluble polymer (B),

for cementing in subterranean formations penetrated by at least a well bore comprising at least the following steps:

(a) preparing an aqueous cement slurry by mixing at least a hydraulic cement, the water-dispersible polymer powder composition (P), and sufficient water to form a pumpable slurry;

(b) placing said aqueous cement slurry through a well bore to a zone to be cemented, and

(c) allowing said aqueous cement slurry to set

wherein additionally 0.5 to 10 wt.-% of at least one non-ionic emulsifier (C) are comprised in the water-dispersible polymer powder composition (P) or added to the aqueous cement slurry.

16. Use according to claim 15, wherein the amount water-dispersible polymer powder composition (P) is from 8 to 15 wt.-%, relating to the cement.

17. Dry cement composition comprising at least

- a hydraulic cement, and
- a water-dispersible polymer powder composition (P) according to any of claims 1 to 8.

18. Dry cement formulation according to claim 17, wherein the amount water-dispersible polymer powder composition (P) is from 8 to 15 wt.-%, relating to the cement.

19. Use according to claim 15, wherein the water-dispersible powder composition (P) and the hydraulic cement are comprised in a dry cement composition, and wherein in step (a) the aqueous cement slurry is prepared by mixing at least the dry cement composition and sufficient water, to form the pumpable slurry.