The present invention relates to the use of polymeric microparticles in hydraulically setting building material mixtures for the purpose of enhancing their frost resistance and cyclical freeze/thaw durability.
ADDITIVE BUILDING MATERIAL MIXTURES CONTAINING IONICALLY
SWOLLEN MICROPARTICLES

[0001] The present invention relates to the use of poly-
meric microparticles in hydraulically setting building ma-
terial mixtures for the purpose of enhancing their frost resis-
tance and cyclical freeze/thaw durability.

[0002] Decisive factors affecting the resistance of concrete
to frost and to cyclical freeze/thaw under simultaneous
exposure to thawing agents are the imperviousness of its
microstructure, a certain strength of the matrix, and the
presence of a certain pore microstructure. The microstruc-
ture of a cement-bound concrete is traversed by capillary
pores (radius: 2 μm-2 mm) and gel pores (radius: 2-50 nm).
Water present in these pores differs in its state as a function
of the pore diameter. Whereas water in the capillary pores
retains its usual properties, that in the gel pores is classified
as condensed water (mesopores: 50 nm) and adsorptively
bound surface water (micropores: 2 nm), the freezing points
of which may for example be well below -50° C. [M. J.
Setzer, Interaction of water with hardened cement paste,
Cemenic Transactions 16 (1991) 415-39]. Consequently,
even when the concrete is cooled to low temperatures, some
of the water in the pores remains unfrozen (metastable
water). For a given temperature, however, the vapor pressure
over ice is lower than that over water. Since ice and
metastable water are present alongside one another simul-
taneously, a vapor-pressure gradient develops which leads to
diffusion of the still-liquid water to the ice and to the
formation of ice from said water, resulting in removal of
water from the smaller pores or accumulation of ice in the
larger pores. This redistribution of water as a result of
cooling takes place in every porous system and is critically
dependent on the type of pore distribution.

[0003] The artificial introduction of microfine air pores in
the concrete hence gives rise primarily to what are called
expansion spaces for expanding ice and ice-water. Within
these pores, freezing water can expand or internal pressure
and stresses of ice and ice-water can be absorbed without
formation of microcracks and hence without frost damage to
the concrete. The fundamental way in which such air-pore
systems act has been described, in connection with the
mechanism of frost damage to concrete, in a large number of
reviews [Sculthorpe, Erdland M. (1998) Ice damage to con-
crete. CRREL Special Report 98-6; S. Chatterji, Freezing of
air-entrained cement-based materials and specific actions of
air-entraining agents, Cement & Concrete Composites 25
(2003) 759-65; G. W. Scherer, J. Chen & J. Valenza,
Methods for protecting concrete from freeze damage, U.S.
Pat. No. 6,485,560 B1 (2002); M. Pigeon, B. Zuber & J.
Marchand, Freeze/thaw resistance, Advanced Concrete
A new process by which cyclic freezing can damage concrete-
the Erolin/Mather effect, Cement & Concrete Research 35

[0004] A precondition for improved resistance of the con-
crete on exposure to the freezing and thawing cycle is that
the distance of each point in the hardened cement from the
next artificial air pore does not exceed a defined value. This
distance is also referred to as the “Powers spacing factor” [T.
C. Powers, The air requirement of frost-resistant concrete,
Proceedings of the Highway Research Board 29 (1949)
184-202]. Laboratory tests have shown that exceeding the
critical “Power spacing factor” of 500 μm leads to damage
to the concrete in the freezing and thawing cycle. In order
to achieve this with a limited air-pore content; the diameter of
the artificially introduced air pores must therefore be less
than 200-300 μm [K. Snyder, K. Natesanier & K. Hover,
The stereological and statistical properties of entrained air voids
in concrete: A mathematical basis for air void systems
characterization, Materials Science of Concrete VI (2001)
129-214].

[0005] The formation of an artificial air-pore system
depends critically on the composition and the conformity of
the aggregates, the type and amount of the cement, the
consistency of the concrete, the mixer used, the mixing time,
and the temperature, but also on the nature and amount of
the agent that forms the air pores, the air entrainer. Although
these influencing factors can be controlled if account is
taken of appropriate production rules, there may never-
theless be a multiplicity of unwanted adverse effects, resulting
ultimately in the concrete’s air content being above or below
the desired level and hence adversely affecting the strength
or the frost resistance of the concrete.

[0006] Artificial air pores of this kind cannot be metered
directly; instead, the air entrained by mixing is stabilized by
the addition of the aforementioned air entrainers [L. Du &
K. J. Folliaard, Mechanism of air entrainment in concrete,
Cement & Concrete Research 35 (2005) 1463-71]. Conven-
tional air entrainers are mostly surfactant-like in structure
and break up the air introduced by mixing into small air
bubbles having a diameter as far as possible of less than 300
μm, and stabilize them in the wet concrete microstructure.
A distinction is made here between two types.

[0007] One type—for example sodium oleate, the sodium
salt of abietic acid or Vinsol resin, an extract from pine
roots—reacts with the calcium hydroxide of the pore solu-
tion in the cement paste and is precipitated as insoluble
calcium salt. These hydrophobic salts reduce the surface
tension of the water and collect at the interface between
cement particle, air and water. They stabilize the
microbubbles and are therefore encountered at the surfaces
of these air pores in the concrete as it hardens. The other
type—for example sodium lauryl sulfate (SDS) or sodium
dodecyl-phenylsulfonate—reacts with calcium hydroxide to
form calcium salts which, in contrast, are soluble, but which
exhibit an abnormal solution behavior. Below a certain
critical temperature the solubility of these surfactants is very
low, while above this temperature their solubility is very
good. As a result of preferential accumulation at the air/
water boundary they likewise reduce the surface tension,
thus stabilize the microbubbles, and are preferably encoun-
tered at the surfaces of these air pores in the hardened
concrete.

[0008] The use of these prior-art air entrainers is accompa-
nied by a host of problems [L. Du & K. J. Folliaard,
Mechanism of air entrainment in concrete, Cement & Con-
crete Research 35 (2005) 1463-71]. For example, prolonged
mixing times, different mixer speeds and altered metering
sequences in the case of ready-mix concretes result in the
expulsion of the stabilized air (in the air pores).

[0009] The transporting of concretes with extended trans-
port times, poor temperature control and different pumping
and conveying equipment, and also the introduction of these
concretes in conjunction with altered subsequent processing,
jerking and temperature conditions, can produce a signifi-
cant change in an air-pore content set beforehand. In the worst case this may mean that a concrete no longer complies with the required limiting values of a certain exposure class and has therefore become unusable [EN 206-1 (2000), Concrete—Part 1: Specification, performance, production and conformity].

The amount of fine substances in the concrete (e.g. cement with different alkali content, additions such as flyash, silica dust or color additions) likewise adversely affects air entrainment. There also may be interactions with flow improvers that have a defoaming action and hence expel air pores, but may also introduce them in an uncontrolled manner.

All of these influences which complicate the production of frost-resistant concrete can be avoided if, instead of the required air-pore system being generated by means of abovementioned air entrainers with surfactant-like structure, the air content is brought about by the admixing or solid metering of polymeric microparticles (hollow microspheres) [H. Sommer, A new method of making concrete resistant to frost and de-icing salts, Betonwerk & Fertigteiltechnik 9 (1978) 476-84]. Since the microparticles generally have particle sizes of less than 100 μm, they can also be distributed more finely and uniformly in the concrete microstructure than can artificially introduced air pores. Consequently, even small amounts are sufficient for sufficient resistance of the concrete to the freezing and thawing cycle.

The use of polymeric microparticles of this kind for improving the frost resistance and cyclical freeze/thaw durability of concrete is already known from the prior art [cf. DE 2229094 A1, U.S. Pat. No. 4,057,526 B1, U.S. Pat. No. 4,082,562 B1, DE 3026719 A1]. The microparticles described therein are notable in particular because they possess a void which is smaller than 200 μm (diameter), and this hollow core consists of air (or a gaseous substance). This likewise includes porous microparticles on the 100 μm scale which may possess a multiplicity of relatively small voids and/or pores.

With the use of hollow microparticles for artificial air entrainment in concrete, two factors proved to be disadvantageous for the implementation of this technology on the market. On the one hand the production costs of hollow microspheres in accordance with the prior art are too high, and on the other hand relatively high added quantities are required in order to achieve satisfactory resistance of the concrete to freezing and thawing cycles.

The object on which the present invention is based was therefore that of providing a means of improving the frost resistance and cyclical freeze/thaw durability for hydraulically setting building material mixtures that develops its full activity even in relatively low added quantities. A further object was not, or not substantially, to impair the mechanical strength of the building material mixture as a result of said means.

Moreover, the effect of this means ought not to be influenced by shorter or longer mixing and processing times, in order to allow harmonized metering of the means.

This object and also further objects not explicitly identified yet readily derivable or comprehensible from the circumstances discussed at the introduction herein are achieved by core/shell microparticles which possess a base-swelling core which has been swollen by means of ionic bases (such as sodium hydroxide, potassium hydroxide or barium hydroxide).

Such particles are produced preferably by emulsion polymerization.

It has been found that these particles of the invention are suitable even in very low added quantities for producing effective resistance towards frost and freeze/thaw cycling.

These microparticles, containing a void, are added to the building material mixture, wherein they remain for a shorter or longer time prior to processing of the mixture. It has been found that the longer the time the microparticles remain in the building material mixture before the mixture cures, the higher the added quantity of microparticles must be in order to achieve the same level of effective resistance towards frost and freeze/thaw cycling.

Surprisingly it has been found that in the case of microparticles swollen with ionic bases in accordance with the invention there is no significant deactivation in binder activity over time.

According to one preferred embodiment the microparticles used are composed of polymer particles which possess a core (A) and at least one shell (B), the core/shell polymer microparticles having been swollen by means of an ionic base.

The preparation of these polymeric microparticles by emulsion polymerization and also their swelling by means of bases such as alkali or alkali metal hydroxides and also ammonia or an amine, for example, are described in European patents EP 22 633 B1, EP 755 29 B1 and EP 388 325 B1.

The core (A) of the particle contains one or more ethylenically unsaturated carboxylic acid (derivative) monomers which permit swelling of the core; these monomers are preferably selected from the group of acrylic acid, methacrylic acid, maleic anhydride, fumaric acid, itaconic acid and crotonic acid and mixtures thereof. Acrylic acid and methacrylic acid are particularly preferred.

The shell (B) is composed predominantly of non-ionic, ethylenically unsaturated monomers. As such monomers use is made preferably of styrene, butadiene, vinyltoluene, ethylene, vinyl acetate, vinyl chloride, vinylidene chloride, acrylo-nitrile, acrylamide, methacrylamide, C1-C12 alkyl esters of (meth)acrylic acid or mixtures thereof. Preference is given to using styrene and/or n-hexyl (meth)acrylate and/or n-butyl(meth)acrylate and/or isobutyl (meth)acrylate and/or propyl(meth)acrylate and/or ethyl methacrylate and/or ethylhexyl(meth)acrylate.

The (meth)acrylate notation here denotes both methacrylate, such as methyl methacrylate, ethyl methacrylate, etc., and acrylate, such as methyl acrylate, ethyl acrylate, etc., and also mixtures of both.

The polymer envelope or shell (B) may further comprise monomers, which enhances the permeability of the shell for the ionic bases. These may be, on the one hand, acid-containing monomers such as acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, monoesters of fumaric acid, itaconic acid, crotonic acid, maleic acid, monoesters of maleic acid, acrylamidoglycolic acid, methacrylamidobenzoic acid, cinnamic acid, vinylacetie acid, trichloroacrylic acid, 10-hydroxy-2-decenonic acid, 4-methacryloyloxyethyl-trimethylenyl acid, styrenecarboxylic acid, 2-(isopropenylcarbonyl-oxy)propylsulfonic acid, 2-(vinylcarbonyl-oxy)ethanesulfonic acid, 2-(isopropenyl-carbonyl-oxy)propylsulfonic acid, 2-(vinylcarbonyl-oxy) propylsulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid.
acid, acrylamidododecanesulfonic acid, 2-propene-1-sulfonic acid, methallylsulfonic acid, styrenesulfonic acid, styrenedisulfonic acid, methacrylamidoethane phosphonic acid, vinylphosphonic acid, and mixtures thereof.

These acid-containing monomers are added to the polymer envelope B preferably in amounts of 0 to 15% by weight (based on the total monomer mixture of the shell), particular preference being given to amounts of 0.2% to 8% by weight; the most preferred are amounts of 0.5% to 4% by weight.

On the other hand the permeability can also be enhanced by means of hydrophilic, nonionic monomers, of which mention may be made here, as examples, of acrylonitrile, (meth)acrylamide, cyanomethyl methacrylate, N-vinylamides, N-vinylformamides, N-vinylacetamides, N-vinyl-N-methyl-acetamides N-vinyl-N-methylformamides, N-methylol-(meth)acrylamide, vinylpyrrolidone, N,N-dimethylpropylacrylamide, dimethylocrylamide, and also other hydroxy-, amino-, amido- and/or cyano-containing monomers and/or mixtures thereof.

These hydrophilic monomers are added to the polymer envelope B preferably in amounts of 0 to 25% by weight (based on the total monomer mixture of the shell), particular preference being given to amounts of 0.5% to 15% by weight; the most preferred are amounts of 1% to 8% by weight.

Hydrophilic and acid-containing monomers together make up preferably not more than 25% by weight in the composition of the polymer envelope (B) (based on the total monomer mixture of the shell); particular preference is given to amounts between 0.2% and 18% by weight, the most preference to amounts between 0.5% and 10% by weight.

In a further preferred embodiment the monomer composition of the core and of the shell does not change with a sharp discontinuity, as is the case for a core/shell particle of ideal construction, but instead changes gradually in two or more steps or in the form of a gradient.

Where the microparticles are constructed as multishell particles, the composition of the shells located between core and outer shell is often oriented to the shells adjacent on either side, which means that the amount of a monomer Mx in general between the amount M(x+1) in the next-outer shell (which may also be the outer shell) and the amount M(x-1) in the next-inner shell (or the core). However, this is not mandatory, and in further particular embodiments the compositions of such intermediate shells may also be freely selected, provided it does not stand in the way of the preparation and the ordered structure of the particle.

Depending on the diameter and the water content, the polymer content of the microparticles employed may be 2% to 98% by weight (weight of polymer relative to the total weight of the water-filled particle).

Preference is given to polymer contents of 5% to 60% by weight, particular preference to polymer contents of 10% to 40% by weight.

The microparticles of the invention can be prepared preferably by emulsion polymerization and preferably have an average particle size of 100 to 5000 nm; particular preference is given to an average particle size of 200 to 2000 nm. The most preferred are average particle sizes of 250 to 1000 nm.

The average particle size is determined by, for example, counting a statistically significant amount of particles by means of transmission electron micrographs.

In the case of the preparation by emulsion polymerization the microparticles are obtained in the form of an aqueous dispersion. Correspondingly, the addition of the microparticles to the building material mixture takes place preferably likewise in this form.

Within the context of the present invention, however, it is also readily possible to add the water-filled microparticles to the building material mixture directly as a solid. For that purpose the microparticles, for example, are coagulated and isolated from the aqueous dispersion by typical methods (e.g. filtration, centrifugation, sedimentation and decanting) and the particles are subsequently dried.

Where addition as a solid is desired or necessary on processing grounds, further preferred drying methods include spray drying and freeze drying.

The water-filled microparticles are added to the building material mixture in a preferred amount of 0.01% to 5% by volume, in particular 0.1% to 0.5% by volume. The building material mixture, in the form for example of concrete or mortar, may in this case include the customary hydraulically setting binders, such as cement, lime, gypsum or anhydrite, for example.

A substantial advantage through the use of the water-filled microparticles is that only an extremely small amount of air is introduced into the concrete. As a result, significantly improved compressive strengths are achievable in the concrete. These are about 25%-50% above the compressive strengths of concrete obtained with conventional air entrainment. Hence it is possible to attain strength classes which can otherwise be set only by means of a substantially lower water/cement value (w/c value). Low w/c values, however, in turn significantly restrict the processing properties of the concrete in certain circumstances.

Moreover, higher compressive strengths may result in it being possible to reduce the cement content of the concrete that is needed for strength to develop, and hence a significant reduction in the price per m³ of concrete.

1. Use of polymeric microparticles, containing a void, in hydraulically setting building material mixtures, characterized in that the core of these particles is swollen by means of ionic bases.

2. Use of polymeric microparticles, containing a void, in hydraulically setting building material mixtures, according to claim 1, characterized in that the base used for swelling is selected from the group of sodium hydroxide, potassium hydroxide, barium hydroxide or a mixture thereof.

3. Use of polymeric microparticles, containing a void, according to claim 1, characterized in that the outer shell may contain acid-containing monomers and/or hydrophilic, nonionic monomers.

4. Use of polymeric microparticles, containing a void, according to claim 3, characterized in that the outer shell contains 0 to 15% by weight, based on the total monomer mixture of the shell, of one or more monomers containing acid groups and/or 0 to 25% by weight, based on the total monomer mixture of the shell, of one or more hydroxy-, amino-, amido- and/or cyano-containing monomers.

5. Use of polymeric microparticles, containing a void, according to claim 3, characterized in that the outer shell contains 0.2% to 8% by weight of one or more acid-
containing monomers and/or 0.5% to 15% by weight of hydrophilic, nonionic monomers.

6. Use of polymeric microparticles, containing a void, according to claim 1, characterized in that the microparticles are composed of polymer particles which comprise a polymer core (A), which is swollen by means of an ionic aqueous base and contains one or more unsaturated carboxylic acid (derivative) monomers, and a polymer envelope (B), which is composed predominantly of nonionic, ethylenically unsaturated monomers.

7. Use of polymeric microparticles, containing a void, according to claim 1, characterized in that the outer shell contains nonionic, ethylenically unsaturated monomers selected from styrene, butadiene, vinyltoluene, ethylene, vinyl acetate, vinyl chloride, vinylidene chloride, acrylonitrile, acrylamide, methacrylamide and/or C1-C12 alkyl esters of acrylic or methacrylic acid.

8. Use of polymeric microparticles, containing a void, according to claim 5, characterized in that the unsaturated carboxylic acid (derivative) monomers of the core A are selected from the group of acrylic acid, methacrylic acid, maleic acid, maleic anhydride, fumaric acid, itaconic acid and crotonic acid.

9. Use of polymeric microparticles, containing a void, according to claim 1, characterized in that the microparticles have a polymer content of 2% to 98% by weight.

8. Use of polymeric microparticles, containing a void, according to claim 1, characterized in that the microparticles have an average particle size of 100 to 5000 nm.

9. Use of polymeric microparticles, containing a void, according to claim 8, characterized in that the microparticles have an average particle size of 200 to 2000 nm.

10. Use of polymeric microparticles, containing a void, according to claim 9, characterized in that the microparticles have an average particle size of 250 to 1000 nm.

11. Use of polymeric microparticles, containing a void, according to claim 1, characterized in that the microparticles are used in an amount of 0.01% to 5% by volume, based on the building material mixture.

12. Use of polymeric microparticles, containing a void, according to claim 11, characterized in that the microparticles are used in an amount of 0.1% to 0.5% by volume, based on the building material mixture.

13. Use of polymeric microparticles, containing a void, according to claim 1, characterized in that the building material mixtures are composed of a binder selected from the group of cement, lime, gypsum and anhydrite.

14. Use of polymeric microparticles, containing a void, according to claim 1, characterized in that the building material mixtures are concrete or mortar.

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