APPLICATION FOR A STANDARD PATENT

ELKEM a/s

Middelthunsgate 27,
Oslo B, Norway

hereby apply for the grant of a Standard Patent

for an invention entitled

"A CONCRETE ADDITIVE COMPRISING A MULTICOMPONENT
ADMIXTURERE CONTAINING MICROSTANICA, ITS METHOD
OF MANUFACTURE AND CONCRETE PRODUCED THEREWITH"

which is described in the accompanying provisional specification.

For a Convention application — details of basic application(s)

<table>
<thead>
<tr>
<th>NUMBER</th>
<th>COUNTRY</th>
<th>DATE OF APPLICATION</th>
</tr>
</thead>
<tbody>
<tr>
<td>824100</td>
<td>NORWAY</td>
<td>7th December, 1982</td>
</tr>
</tbody>
</table>

For an application made by virtue of section 51

Original Application No.______

by

request that the Patent may be granted as a Patent of Addition

the Patent applied for on Application No.

as

Patent No.______

in the name of

request that the term of the Patent of Addition be the same as that for the main invention or so much of the term of the patent for the main invention as is unexpired.

My address for service is COLLISON & CO., Patent Attorneys, Savings Bank Building, 97 King William Street, Adelaide, South Australia, 5000.

Dated this 7th day of December, 1983

ELKEM a/s,

By their Patent Attorneys,

COLLISON & CO.

(G.E. HABEL

(Signature)

TO:

THE COMMISSIONER OF PATENTS

This form must be accompanied by either a provisional specification (Form 9 and true copy) or by a complete specification (Form 10 and true copy).

COMMONWEALTH OF AUSTRALIA
Patents Act 1952–1969

COMPLETE SPECIFICATION

(ORIGINAL)
DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention application made for a patent for an invention entitled: "A CONCRETE ADDITIVE COMPRISING A MULTI-COMPONENT ADMIXTURE CONTAINING MICROSILICA, ITS METHOD OF MANUFACTURE AND CONCRETE PRODUCED THEREWITH"

We, Arne G. Arnesen and Per Goller, Vice Presidents

of Elkem a/s, Middelthunsgate 27, Oslo 3, Norway

do solemnly and sincerely declare as follows:

1. I am the applicant for the patent
   We are authorized by Elkem a/s, the applicant, for the patent to make this declaration on its behalf.

2. The basic application as defined by section 141 of the Act was made in Norway on the 7th day of December, 1982, by Elkem a/s.

3. Magne Bøtøl

Marvikveien 91, 4600 Kristiansand, Norway

is the actual inventor of the invention and the facts upon which the applicant is entitled to make the application are as follows:

The applicant is the assignee of the actual inventor.

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

   (For an earlier application made in a Convention country to be disregarded, see section 143AA of the Act.)

(A) An earlier application in respect of the invention the subject of the application was made in

   (Here set out the earlier application in the order of the dates of publication or registration of the earlier application.)

      A request has been made to you under section 142AA of the Patents Act 1952 to disregard the earlier application referred to in paragraph 2 of this Declaration.

      (Here set out in reverse order the dates of the applications referred to in paragraph 2 of this Declaration.)

    Except as stated in this paragraph, the basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

Declared at Oslo this 23rd day of November, 1983

For and on behalf of Elkem a/s

Arne G. Arnesen Per Goller

(Signature of Declarant)

THE COMMISSIONER OF PATENTS.

(IMPORTANT – Cross out applicable words in above Form.)
MICROSILICA ADDITIVE FOR CONCRETE

ELKEM a/s

AU-A-22159/83 7.12.83
824100 7.12.82 NO
14.6.84

C04B 13/22
C04B 13/20
C04B 7/35
MAGNE DÅSTØL
CO

Claim

1. A cement or mortar additive comprising microsilica in an amount of 30% to 98% by weight and a non-high range water-reducing agent and/or a high-range water-reducing agent present in an amount of from 2.0% to 50% by weight based on the weight of microsilica.

12. A hardened concrete structural element which is formed of concrete batch materials to which has been added an admixture comprising a non-high-range water-reducing agent and/or a high-range water-reducing agent dispersed in microsilica in which the microsilica in the structural element is present in an amount from about 2% to about 100% of microsilica by weight based on the weight of cement in the structural element and the said at least one ingredient being present in said structural element in an amount from about 0.1% to about 5.0% by weight based on the weight of cement in the structural element.

.../2

ND 2 34

105/32/15
15. A process of forming a multicomponent admixture additive for concrete, which process comprises the steps of mixing a non-high-range water-reducing agent and/or a high-range water-reducing agents with microsilica in an amount to provide from about 30% to about 98% by weight of said admixture and adding from about 2.0% to about 50% by weight based on the weight of microsilica of the water-reducing agent in the admixture and continuing the mixing until the water-reducing agent is uniformly dispersed in the microsilica.
A CONCRETE ADDITIVE COMPRISING A MULTICOMPONENT ADMIXTURE CONTAINING MICRO SILICA, ITS METHOD OF MANUFACTURE AND CONCRETE PRODUCED THEREWITH.
A CONCRETE ADDITIVE COMPRISING A MULTICOMPONENT ADMIXTURE CONTAINING MICRO SILICA, ITS METHOD OF MANUFACTURE AND CONCRETE PRODUCED THEREWITH.

The present invention relates to an additive for concrete which comprises a multicomponent admixture that contains microsilica and at least one non-high range water-reducing agent or at least one high-range water-reducing agent. Advantageously, the admixture may contain one or more non-high range water-reducing agents in combination with one or more high-range water-reducing agents along with the microsilica. Accelerators and retarders alone or in combination may also be used in the admixture as optional ingredients.

As one example, the invention is directed to overcome the drawback associated with degradation of the air-void system of entrained concrete which results from the use of water reducers while at the same time other known advantages such as workability, strength and formability of concrete which contains water-reducing agents are substantially maintained. In accordance with the present invention, the microsilica and at least one water-reducing agent with or without additional optional ingredients are pre-mixed and the resulting admixture is added and mixed into the concrete batch at any desired stage. The premixing is of great advantage as compared to the conventional practice of adding each ingredient separately to the
2. concrete batch in that the action of the water-reducing agent during premixing tends to uniformly coat and homogeneously disperse the microsilica particles with resulting breakdown of flocs of material. The flocs of material that tend to form when the ingredients are separately added in conventional practice can be a serious drawback to desirable uniform strength and durability of the cast concrete. Once flocs are formed in the concrete batch, it requires prolonged mixing to disperse the flocs and over mixing may be deleterious to the workability and formability of the batch.

While the mechanism of premixing is not completely understood, it is believed to provide a synergistic effect in the plasticity and workability of the concrete batch along with increased strength over ordinary concrete batches to which the ingredients are separately added in conventional practice.

The water-reducing agents and the optional accelerators and retarders of the present invention may be well-known conventional materials currently used in high strength concrete which may have a compressive strength of up to about 6,000 to 12,000 pounds per square inch (4.14 x 10⁷ to 8.27 x 10⁷ N/m²).

One of the greatest advances in concrete technology in recent decades has been the advent of air entrainment to protect concrete from damage caused by the freezing and thawing
3.

and when it contains de-icing chemicals. The use of entrained air is generally recommended in concrete for almost all applications. Tests have shown that concrete containing about 5 to 7.5%, \( \pm 1\% \), percent by volume air content will withstand up to about 1900 freeze-thaw cycles as contrasted to a maximum of about 150 cycles of non-air entrained concrete which is identical in all other respects. See for example, "Air-Entrained Concrete", Portland Cement Association, Document ISO 45.027, 1967.

There are many other benefits from the use of air entrained concrete including improved workability, increased resistance to de-icers such as calcium chloride, increased sulphate resistance, and improved water tightness.

One widely used method of making air entrained concrete includes the step of adding an air-entraining material during the mixing of the concrete. Experience has indicated that the mixing action is the most important factor in the production of air-entrained concrete and in this regard uniform distribution of entrained air voids is essential to the production of scale-resistance concrete; non-uniformity is always a risk if the entrained air is inadequately dispersed during mixing. Such factors as the batch size of the concrete being mixed, the condition of the mixer and the rate of mixing are also important. Over mixing may even result in a loss of some of the entrained air but the techniques and preferred procedures associated with the mixing
4. The phase of air entrained concrete are now rather widely understood, and further amplification is considered unnecessary for those skilled in the art.

5. A number of air-entraining materials manufactured from a variety of materials are commercially available today such as thermoplastic resins containing phenol, aldehyde and ether groups and the salts and soaps thereof.

10. Vinsol resins are undoubtedly the most widely used air-entraining materials in the United States. Vinsol resin is a thermoplastic resin derived from pine wood and containing phenol, aldehyde and ether groups. The sodium soap of Vinsol resin is a particularly effective air-entraining material and only about 0.15% by weight of cement need be used for entraining air in a concrete batch in conventional manner. DAREX AEA which is a sulphonated hydrocarbon acid derivative of fats and greases sold by Dewey and Almy Chemical Co. is another widely used air-entraining agent.

15. The air-entrained concrete which results from the use of recognized air-entraining products contains a large number of air bubbles of an extremely small size; average bubble diameter usually ranges from three thousandths to six thousandths of an inch (76.2 to 152.4) microns and as many as three hundred to five hundred billion bubbles may be present in a cubic yard (230 to 380 billion per cubic metre) of air-entrained concrete having an air...
content in the range of four to six percent by volume, and one and one-half inch (3.8 cm) maximum sized aggregate. The bubbles are not interconnected and are well distributed throughout the cement/water phase. The spacing of the air voids is an important factor in the freeze-thaw durability of hardened concrete, and a spacing of less than 0.008 inches (20 microns), as measured by ASTM C457 standard is considered essential for the attainment of the requisite freeze-thaw resistance.

One of the most significant developments in concrete since air-entrained concrete was developed in the mid-1930's is the use of so-called water-reducing agents.

Water-reducing agents are chemical compounds which, when added to concrete, fluidize the concrete for a period of time so that normal workability can be obtained in concrete having much lower water-content ratios than would normally be employed or (2) extremely workable "flowing concrete" (that is essentially self-levelling without undesirable side effects, such as segregation, low-durability, low abrasion resistance and bleeding). can be obtained, or (3) a combination of (1) and (2).

Non-high-range water-reducing agents are well-known additives for concrete. The commercial materials generally available fall into six different classes:
6.

1. Hydroxylated carboxylic acids and their salts,
2. Modifications and derivatives of hydroxylated carboxylic acids and their salts,
3. Inorganic materials such as zinc salts, borates, phosphates and chlorides,
4. Carbohydrates, polysaccharides and sugar acids,
5. Amines and their derivatives and polymeric compounds such as cellulose ethers and silicones,

The terms non-high-range water-reducing agent and non-high range water-reducer as used herein are intended to mean one or more of the ingredients in the five foregoing classes of conventional materials alone or in combination or any other ingredient having an equivalent effect.

15. The high-range water-reducing agents in widespread commercial use today include:

1. Lignosulphonic acids and their salts and modifications and derivatives thereof,
2. Melamine derivatives,

The terms high-range water-reducing agent and high-range water reducer as used herein are intended to mean one or more of the ingredients in the foregoing three classes of materials alone or in combination or any other ingredient having an equivalent effect.
There are at least twelve widely used high-range water-reducing agents, eight of which belong to the above categories (2) and (3). The preferred material in category (2) is a conventional sulphonated condensate of melamine and formaldehyde sold under the brand name of "Melment" and the preferred material in category (3) is a sulphonated condensate of naphthalene and formaldehyde.

The high-range water-reducing agents have a much greater plasticizing effect in conventional concrete batches. Good results in workability, formability and strength have been achieved with the high-range water-reducing agents usable in the present invention.

Concrete containing high-range water-reducing agents is extensively used in cast-in-place concrete work where extreme flowing characteristics are required such as in areas of high density of reinforcement, pumping and in complicated form work. Among the advantages of the use of high-range water-reducing agents in pre-cast and ready-mix concrete are (a) increased strength at all ages, (b) improved resistance to attack by sulphates, (c) increased bonding to reinforced steel, (d) improved workability and formability and (e) reduced permeability to water penetration.
When a high-range water-reducing agent is added to a concrete mix, the plasticizing effects last for approximately 30-60 minutes, depending on the job conditions. Consequently it should be added at the job site when used in ready-mixed concrete.

Concrete with one or more high-range water-reducers therein are set out in "Super Plasticized Concrete", ACI Journal, May 1977, pp. N6-N11 inclusive, and the references set out therein.

Although concrete which may be classified as either air entrained or plasticized with water-reducer has proved eminently feasible for many applications requiring only the qualities attributable to air entrainment or plasticization, difficulties have been encountered when the contractor has attempted to use both an air-entraining admixture and a high-range water-reducer to plasticize the concrete.

Specifically, it is today universally accepted that the air-void system of hardened air-entrained concrete containing a high-range water-reducing agent and neutralized vinsol resin is very poor; that is, the air-void spacing factor is greater than 0.008 inches (20 microns) and there is a potential for losing air from the fresh concrete. As mentioned, the air-void parameters, and specifically the spacing factor of the air-void system, is a major criterion for predicting the probable performance of concrete to withstand repeated freeze-thaw cycling.

The problem, then, faced by the industry is to produce a concrete which possesses the desirable freeze-thaw and allied characteristics of air entrained concrete, together with the excellent workability and increased strengths of water-reducer
plasticized concrete.

The invention enables the provision of a water-reducer plasticizing additive for concrete which will not reduce but will enhance freeze-thaw resistance.

It has been found that a premixed admixture of microsilica and one or more water-reducing agents, preferably a high-range water-reducing agent used alone or in combination, when added to mortar and concrete increases the density and impermeability of that mortar and concrete by several orders of magnitude. Indeed, it has been learned that non-air entrained concrete produced with the microsilica admixture of the present invention is virtually impermeable to the ingress of freezeable water and aggressive fluids. Concrete containing the microsilica admixture possesses freeze-thaw resistance equal to or better than concrete having proper air entrainment and it is of equal or higher strength. Thus, deterioration of the air-void system normally experienced with water-reducing agents both ordinary and high-range is of no concern since loss of air or increase in bubble spacing is overcome by the beneficial effects of the microsilica admixture with respect to fundamental changes in the pore structure of the binder phase of the concrete. More specifically, there results a more uniform dispersion of the binder phase having a significantly finer pore structure.

According to a first aspect of the invention, there is provided a cement or mortar additive comprising microsilica in an amount of from 30% to 98% by weight and a non-high range water-reducing
agent and/or a high-range water-reducing agent present in an amount of from 2.0% to 50% by weight based on the weight of microsilica.

The microsilica used in the present invention is an amorphous silica by-product of the manufacture of ferrosilicon and also silicon metal produced by capturing the finely divided particles from stack gases of electric arc furnaces. Microsilica is a pozzolan, i.e., it combines with lime and moisture at ordinary temperatures to form compounds having cementitious properties. The main constituent is silicon dioxide (SiO\textsubscript{2}) and it is usually present in at least about 60% but best results are achieved in the present invention when the SiO\textsubscript{2} content is at least about 85% by weight.

An amorphous silica that is eminently suitable for use in the present invention is obtained as a by-product in the production of silicon metal or ferrosilicon in electric reduction furnaces. In these processes, fairly large quantities of silica are formed as dust which is recovered in filters or other collection apparatus. Such silica can be obtained from Elkem a/s, Norway.

The analyses and physical data for typical samples of silica of this description are given in the following tables:
<table>
<thead>
<tr>
<th>Component</th>
<th>% by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>94 - 98</td>
</tr>
<tr>
<td>SiC</td>
<td>0.2 - 0.7</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.05 - 0.15</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.01 - 0.02</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.1 - 0.3</td>
</tr>
<tr>
<td>MgO</td>
<td>0.2 - 0.8</td>
</tr>
<tr>
<td>CaO</td>
<td>0.1 - 0.3</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.3 - 0.5</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.2 - 0.6</td>
</tr>
</tbody>
</table>

**TABLE 1**

Dust collected in bag filter from production of 75% FeSi.
12.

<table>
<thead>
<tr>
<th>Component</th>
<th>% by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>0.003 - 0.01</td>
</tr>
<tr>
<td>Cu</td>
<td>0.002 - 0.005</td>
</tr>
<tr>
<td>Zn</td>
<td>0.005 - 0.01</td>
</tr>
<tr>
<td>Ni</td>
<td>0.001 - 0.002</td>
</tr>
<tr>
<td>S</td>
<td>0.1 - 0.3</td>
</tr>
<tr>
<td>P</td>
<td>0.03 - 0.06</td>
</tr>
<tr>
<td>Ignition loss (1000°C)</td>
<td>0.8 - 1.5</td>
</tr>
<tr>
<td>Bulk density, from bunker, g/l</td>
<td>200 - 300</td>
</tr>
<tr>
<td>Bulk density, compacted, g/l</td>
<td>500 - 700</td>
</tr>
<tr>
<td>Real density, g/cm³</td>
<td>2.20 - 2.25</td>
</tr>
<tr>
<td>Specific surface, m²/g</td>
<td>18 - 22</td>
</tr>
<tr>
<td>Primary particle size, percentage &lt;1 µm</td>
<td>90</td>
</tr>
</tbody>
</table>
### TABLE 2

Dust collected in bag filter from production of 75% FeSi:

<table>
<thead>
<tr>
<th>Component</th>
<th>% by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>86 - 90</td>
</tr>
<tr>
<td>SiC</td>
<td>0.1 - 0.4</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.3 - 0.9</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.02 - 0.06</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.2 - 0.6</td>
</tr>
<tr>
<td>MgO</td>
<td>2.5 - 3.5</td>
</tr>
<tr>
<td>CaO</td>
<td>0.2 - 0.5</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.9 - 1.8</td>
</tr>
<tr>
<td>K₂O</td>
<td>2.5 - 3.5</td>
</tr>
<tr>
<td>Component</td>
<td>% by Weight</td>
</tr>
<tr>
<td>---------------------------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>0.2 - 0.4</td>
</tr>
<tr>
<td>C</td>
<td>0.8 - 2.0</td>
</tr>
<tr>
<td>P</td>
<td>0.03 -</td>
</tr>
<tr>
<td>Ignition loss (1000°C)</td>
<td>2.4 - 4.0</td>
</tr>
<tr>
<td>15. Bulk density, from bunker, g/l</td>
<td>200 - 300</td>
</tr>
<tr>
<td>Bulk density, compacted, g/l</td>
<td>500 - 700</td>
</tr>
<tr>
<td>Real density, g/cm³</td>
<td>2.20 -</td>
</tr>
<tr>
<td>20. Specific surface, m²/g</td>
<td>18 - 22</td>
</tr>
<tr>
<td>Primary particle size, percentage &lt; 1 μm</td>
<td>90</td>
</tr>
</tbody>
</table>
Amorphous silica of the above type can be obtained from other manufacturers of Si and FeSi, for example, the manufacture of silicon involves the reduction of silica (coarse, silica, e.g. quartz) with carbon. Iron is added if the alloy ferrosilicon is to be manufactured. Part of the product of this reduction of silica may be re-oxidized in the vapour phase (e.g. in air) to form the fine, particulate silica that is useful herein. While the dust collected from an electric furnace producing ferrosilicon containing at least 75% silicon is preferred, the dust collected from an electric furnace used to produce 50% ferrosilicon may also be used in accordance with the present invention.

It is possible to obtain the amorphous silica not as a by-product but as the major product, by appropriately adjusting the reaction conditions. Amorphous silica of this type may also be produced synthetically without reduction and re-oxidation.

The amorphous silica used in the present invention is composed substantially of sub-micron, spherical particles. The spherical shape together with its fineness and pozzolanic activity makes it surprisingly useful in accordance with the present invention.

For example, the amorphous silica particles may consist of at least 60 to 90% by weight of SiO₂, will have a real density of 2.20-2.25 g/cm³ and will have a specific surface area of 18-22 m²/g, the particles being substantially spherical and wherein at least 90% by weight of the primary...
particles have a particle size of less than 1 micron. Of course, variation of these values is readily possible. For example, the silica may have a lower SiO₂ content. Moreover, the particle size distribution can be adjusted; thus, it is possible to remove coarser particles by classification.

The amorphous silica may be dark grey in colour owing to a content of carbon. However, this carbon can be burnt off, e.g. at temperatures of above 400°C. It is also possible to modify the silicon and ferrosilicon manufacturing processes as to obtain the silica in a comparatively white form which is otherwise virtually identical with the grey silica normally produced. Essentially, the process modification consists of reducing the amount of coal in, or eliminating coal from, the charge. The other consequence of this modification is a change in the proportion of silica produced to the amount of silicon or ferrosilicon; in other words the ratio of silica to silicon or ferrosilicon is higher in the modified process.

The term microsilica as used herein is intended to mean the particulate amorphous silica obtainable by a process in which silica is reduced and the reduction product is oxidized in the vapour phase in air. The said term microsilica also includes the same type of amorphous silica produced synthetically without reduction and re-oxidation. Most conveniently, the microsilica used in the present invention is obtained from the off-gas of silicon metal or ferrosilicon produced in electric reduction furnaces.
17.

The admixture of the present invention comprises from about 30% to about 98% by weight of microsilica and from about 2% to 50% of one or more water-reducing agents, which may be high-range water-reducing agents, based on the weight of the microsilica in the admixture. One or more high-range water-reducing agents may be used either alone or in combination with one or more ordinary or non-high-range water-reducing agents. These are the essential ingredients in the microsilica admixture in which the selected high-range or ordinary water-reducing agent is preferably uniformly and homogeneously dispersed in the microsilica.

The ingredients may be mixed in any conventional mixing apparatus and in one example 50 pounds (22.7 kg) of microsilica and 5 pounds of Mel-ment high-range water reducing agent are fed to a rotary dry batch drum type blender to disperse uniformly and homogeneously the particulate ingredients in intimate contact in the admixture in accordance with the present invention. Best results are achieved by mixing the essential ingredients in aqueous slurry to ensure intimate contact between the ingredients and a uniform homogeneous dispersion. The aqueous slurry may comprise from about 10% to 80% by weight microsilica and preferably from about 40% to about 60% by weight of microsilica and from about 0.5% to about 40% by weight (dry weight) of one or more high-range or ordinary water-reducing agent alone or in combination and preferably from about 1.0% to about 20% by weight of the water-reducing agent alone or in combination therein, the balance being water.
In one example 45 pounds (20.4 Kg) of microsilica, 3 pounds (1.36 Kg) of commercial grade of sulphonated-condensate of naphthalene formaldehyde (high-range water-reducing agent) and 3 pounds (1.36 Kg) of a commercial grade of cellulose ether (water-reducing agent) are uniformly and homogeneously dispersed in 5.5 US gallons (20.8 dm$^3$) of water preferably in a Banbury mixer.

The pH of the aqueous slurry may be adjusted with conventional mineral acid or alkali to between about 3.0 to about 7.5 and preferably between about 5.0 to about 6.0 in order to obtain a slurry of proper consistency for transportation and mixing into the concrete batch. In addition or instead of adjusting the pH of the slurry one may use dispersing agents such as phosphates, citric acid, polyacrylates or glycerine in order to obtain the desired slurry consistency. Water is the most economical liquid to use in forming the admixture slurry of the present invention—but, if desired, an organic liquid may be employed provided that it is compatible with the concrete and is not otherwise deleterious.

Relative viscosity of aqueous slurry admixture of the present invention were recorded using a Haake viscometer utilizing an E.30 sensor and the standard procedure described by the manufacture and compared to a blank aqueous slurry containing the same amount of microsilica without any water-reducing agent. On each sample the slurry contained 0.65% by weight of microsilica for comparison.

The following data was recorded in these tests:
<table>
<thead>
<tr>
<th>Sample</th>
<th>Inverse speed of sensor rotation</th>
<th>1 HR measured Torque</th>
<th>7 days measured Torque</th>
<th>28 days measured Torque</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>32</td>
<td>53</td>
<td>&gt;150</td>
<td>&gt;150</td>
</tr>
<tr>
<td></td>
<td>16</td>
<td>56</td>
<td>&gt;150</td>
<td>&gt;150</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>60</td>
<td>&gt;150</td>
<td>&gt;150</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>64</td>
<td>&gt;150</td>
<td>&gt;150</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>69</td>
<td>&gt;150</td>
<td>&gt;150</td>
</tr>
<tr>
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<td>1</td>
<td>78</td>
<td>&gt;150</td>
<td>&gt;150</td>
</tr>
<tr>
<td>Yield Point</td>
<td>49</td>
<td>&gt;150</td>
<td>-150</td>
<td>-150</td>
</tr>
<tr>
<td>Sample -A- Ligno sulphonate</td>
<td>32</td>
<td>4</td>
<td>8</td>
<td>11</td>
</tr>
<tr>
<td>2.5% by weight (Borresperse NA)</td>
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<td>11</td>
<td>16</td>
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<tr>
<td></td>
<td>8</td>
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<td>17</td>
</tr>
<tr>
<td></td>
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<td>6</td>
<td>12</td>
<td>18</td>
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<tr>
<td></td>
<td>2</td>
<td>7</td>
<td>14</td>
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<tr>
<td></td>
<td>1</td>
<td>9</td>
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<tr>
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<td>2</td>
<td>3.5</td>
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<tr>
<td>Sample -B- Sulphonated condensate of naphthalene and formaldehyde</td>
<td>32</td>
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<td>17</td>
<td>26</td>
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<td>2.5% by weight (Mighty)</td>
<td>16</td>
<td>20</td>
<td>21</td>
<td>27</td>
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</tr>
<tr>
<td></td>
<td>1</td>
<td>39</td>
<td>34</td>
<td>33</td>
</tr>
<tr>
<td>Yield Point</td>
<td>28</td>
<td>28</td>
<td>43</td>
<td></td>
</tr>
<tr>
<td>Sample -C- sulphonated condensate of melamine and formaldehyde</td>
<td>32</td>
<td>21</td>
<td>57</td>
<td>55</td>
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<tr>
<td>2.5% by weight (Rescon H P)</td>
<td>16</td>
<td>32</td>
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<td>61</td>
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<td></td>
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<td>Yield Point</td>
<td>32</td>
<td>63</td>
<td>72</td>
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As shown in the foregoing date microsilica will tend to form a thixotropic mixture in water which frequently results in a gelling of the aqueous slurry. When the slurry gels it is not satisfactory since as a practical matter it is extremely difficult to pump from storage. It was quite surprising and unexpected to find that the high-range water-reducing agent of samples B and C above and ordinary water-reducing agent of sample A above were effective to reduce the tendency for the aqueous slurry to gel as is often experienced with microsilica alone in aqueous slurry.

It is believed that during mixing the high-range and ordinary water-reducing agents tend to coat the surface of the microsilica particles and thereby effectively reduced the tendency for the slurry to gel. Experience has shown that when the yield point in the above table is in the neighbourhood of about 25 the aqueous slurry is excellent for use in accordance with the present invention and the aqueous slurry is satisfactory up to a yield point of about 75. When the yield point of the slurry is above about 100 it becomes difficult to pump and the slurry tends not to be satisfactory for use in accordance with the present invention.

In accordance with the present invention aqueous slurries of microsilica are stabilized and the tendency to gel may be materially reduced or eliminated by dispersing from about 0.1% to about 10.0% and preferably from about 2.0% to 5.0% of high-range or ordinary water-reducing agent by weight (dry-basis) based on the weight of microsilica in the aqueous slurry. In general, the amount
of microsilica in the aqueous slurry will comprise from about as little as 5% and up to about 80% by weight. One or more high-range or ordinary water-reducing agents may be used alone or in combination in order to stabilize the microsilica aqueous slurry admixture. When the aqueous slurry admixture is to be used as an additive for concrete or mortar the amount of high-range or ordinary water-reducing agent may exceed 10% by weight and as specified herein above may constitute from about 0.5% to about 40% by weight of the aqueous slurry.

The amount of admixture of the present invention to be added to conventional fresh concrete mixture or mortar will vary depending upon the application at hand. The amount of admixture to be added is based on the weight of cement in the concrete or mortar batch.

In general, a sufficient quantity of the admixture of the present invention is added and mixed into fresh concrete or mortar batch to provide therein from about 2.0% to about 100% and preferably from about 2% to 25% by weight of dry microsilica based on the weight of cement in the concrete batch and from about 0.1% to about 5% by weight of high-range or ordinary water-reducing agent alone or in combination based on the weight of cement in the concrete or mortar batch.

In accordance with standard industry practice, the optimum amount of the ingredients in the admixture and the amount of admixture within the specified range to be added to the concrete with the job materials at hand is determined by tests that simulate the ambient conditions and construction procedures to be encountered on the construction job. Conventional tests are employed to indicate the effect of the admixture on the concrete insofar as pertinent to the job with respect
to air content of the concrete, consistency, bleeding of water and possible loss of air from fresh concrete, rate of hardening, compressive and flexural strength, resistance to freezing and thawing, shrinkage on drying and permissible chloride content.

The conventional addition of high-range and ordinary water-reducing agents frequently cause the concrete batch to bleed excessively and segregate as indicated by a thin watery paste which fails to hold the coarse aggregate particles in suspension. It is also known that most high range and ordinary water-reducing agents tend to effect plasticization by reducing the surface tension of the water component of the concrete mixture. This may result in separation of coarse aggregate particles and result in low freeze-thaw resistance, loss of pumpability, poor abrasion resistance, difficulty in the finishing operation and poor surface texture in form work.

The addition of microsilica from the admixture of the present invention with its high degree of fineness increases the surface area of the solids per unit of water volume, thus achieving better separation and suspension of coarse aggregate particles and results in increased plasticity and workability through change in particle interference. Since the mixture of cement, water and admixture of the invention contains more solids per unit volume, the paste is less watery and less inclined to separate. Bleeding is thereby reduced by the microsilica by holding the water in paste. This results in a homogeneous, high-workable, pumpable mixture with reduced bleeding characteristics.
23.

Compressive strength achieved by concrete containing the admixture of the present invention is generally higher than one would expect from the addition of increments of strength gained through the addition of each ingredient separately. The reason for this is not fully understood but it is believed that the high-range or ordinary water-reducing agent gives better distribution throughout the concrete mass to the microsilica particles and that certain synergistic effects exist between the admixture ingredients.

The admixture of the present invention is used to advantage in conventional fresh concrete mixes and is mixed into the concrete mass using the conventional techniques now employed for mixing concrete batches. For example, an aqueous slurry admixture containing 45 pounds (20 kg) of microsilica, 8 pounds (3.6 kg) of dry Lomar D (high-range water-reducing agent, sulphonated condensate of naphthalene and formaldehyde) and 5.5 gallons (20.8 dm$^3$) of water may be added and mixed into a conventional fresh concrete batch containing 450 pounds (204 kg) of Portland cement Type I without any other additive. The resulting concrete mixture at a water to cement ratio of 0.35 by weight has good workability, consistency and no segregation in the fresh state. In the hardened state, the 28 days compressive strength is typically high and of the order of 12,000 p.s.i. (8.27 x 10$^7$ N/m$^2$) and the freeze-thaw resistance is surprisingly high even in the absence of air entrainment. The concrete mixture contains 10% microsilica (dry) and about 1.5% of Lomar D (dry)
based on the weight of cement in the concrete mix. The decreased permeability of the resulting mixture increases the resistance to ingress of water and aggressive chemicals with a resulting improvement in freeze-thaw characteristics compared to a concrete or mortar mixture that do not include said microsilica aqueous slurry admixture.

The admixture of the present invention is premixed in optimum portions as determined by standard industry tests to provide a single dispensing system as compared to conventional practice where three to four dispensing systems are required at the job site. Dispensing of all additives may be carried out simultaneously with the admixture of the present invention in which the ingredients are in uniform and homogeneous dispersion as compared to the conventional practice of adding the separate ingredients sequentially in order to avoid flocculation. The admixture of the invention saves on truck loading time and reduces error in that only one batch addition is required rather than three or four. Storage facilities are reduced and quality control is increased by having a single manufacturer supply all additives in the single admixture of the present invention which eliminates the problem of storage tank contamination. Another advantage of the aqueous slurry form of admixture of the present invention is that it eliminates fine particle dust at the job site. Although on smaller jobs, the dry particulate admixture may be packaged in 80 to 100 pound (36.2 to 45.4 kg) bags and delivered to the job site.
The ability of the admixture of the present invention to impart increased sulphate resistance and increased resistance to alkali-silica reaction in concrete containing it, will be realized from the beneficial effects of microsilica added to the concrete mixture.

Since the admixture of the present invention may be used in conditions which may lengthen setting time to an objectionable degree, accelerating ingredients may be added to the admixture to provide optimum setting and early strength gain characteristics. Further, it may be desirable to retard the setting time of the fresh concrete as for example in a bridge deck so that hardening takes place after the placing and finishing operations are completed.

An admixture in accordance with the present invention may be tailor-made with optimum ingredients and amounts of ingredients for the concrete to be used in the construction job at hand. Any of the known additives conventionally used in batching concrete or mortar may be incorporated into the admixture of the present invention.

Accelerators such as the known calcium chloride, calcium nitrate and calcium formate may be incorporated into the admixture with the essential ingredients in amounts that are currently used in the industry as determined by standard test for optimum quantity for the application at hand. One or more accelerators will comprise from about 5% to about 20% by weight based on the weight of microsilica in the admixture.

Retarders such as sugar in the form of glucose or sucrose conventionally used in concrete
or mortar batches may also be incorporated in
the admixture in optimum amounts as determined
by standard testing. One or more retarders
may be present in an amount of from about 5%
to about 20% by weight based on the weight of micro-
silica in the admixture.

If desired, air entraining agents such as
Vinsol resin or Darex which is a sulphonated fatty
acid derived from fats and greases may be incorporated
into the admixture of the present invention in those
particular applications where a given level of
entrained air may be a desirable characteristic. One
or more air entraining agents may be present in
an amount of from about 0.5% to about 2% by weight
based on the weight of microsilica.

Any one or more additives alone or in
combination with other additives may be incor-porated
with the essential ingredients in the admixture
of the present invention. Compatibility and
consistency of the admixture is determined by
routine standard testing as well as the final effect
on the particular concrete or mortar batch to be
used in the construction job at hand.

The admixture of the present invention may
contain various proportions of the selected in-
gredients but the benefit of the present invention
may be realized if the amount of admixture mixed
into a conventional fresh concrete batch will
be sufficient to provide from about 2.0% to about
100% by weight of microsilica based on the weight
of cement and from about 0.1% to about 5% by weight
of one or more of the high-range or ordinary water-
reducing agents alone or in combination based on
the weight of the cement. Water or an organic
liquid compatible with fresh concrete is preferably added to the admixture in an amount sufficient to provide slurry with the essential ingredients uniformly and homogeneously dispersed therein. Accelerators, retarders, air entraining agents and any other conventional additives may be mixed with the essential ingredients of the admixture of the present invention in an amount sufficient to provide the desired concentration in the fresh concrete batch. In all cases the optimum amount of ingredients present in the admixture of the present invention is determined by standard conventional testing under the simulated ambient conditions for the job material at hand and construction procedures to be used.
and will have a specific surface area of 18-22 m²/g, the particles being substantially spherical and wherein at least 90% by weight of the primary.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A cement or mortar additive comprising microsilica in an amount of 30% to 98% by weight and a non-high-range water-reducing agent and/or a high-range water-reducing agent present in an amount of from 2.0% to 50% by weight based on the weight of microsilica.

2. An additive as claimed in Claim 1 slurried in water and/or an organic liquid to provide from 20% to 80% by weight of solids in the slurry.

3. An additive as claimed in Claim 1, which includes one or more non-high-range water-reducing agents and one or more high-range water-reducing agents.

4. An additive as claimed in Claim 1, 2 or 3 which includes one or more accelerators, one or more retarders and/or one or more air entraining agents.

5. An additive as claimed in any one of Claims 1 to 4 in which the microsilica is obtained from the off-gas of an electric furnace used to produce ferrosilicon or silicon metal.

6. A cement or mortar additive comprising an aqueous slurry containing a non-high-range water-reducing agent and/or a high-range water reducing
agent dispersed in the slurry and mixed with microsilica, having a slurry solids content of the microsilica and the water-reducing agent of from 20% to 80% by weight (the weight of the microsilica and the weight of the water-reducing agent both being measured on a dry basis), of which the microsilica is present in an amount of at least 10% by weight of the solids content of the slurry and in which the water-reducing agent is present in an amount of from 0.4% to about 40.0% of the solids content therein:

7. An aqueous slurry as claimed in Claim 6 having a pH of from 3.0 to 7.5.

8. An aqueous slurry as claimed in Claim 6 or 7 in which the microsilica and the water-reducing agent are uniformly and homogeneously dispersed in suspension in said slurry.

9. An aqueous slurry as claimed in Claim 6, 7 or 8 which includes one or more non-high-range water-reducing agents and one or more high-range water-reducing agents.

10. An aqueous slurry as claimed in any one of Claims 5 to 9 in which the microsilica is obtained from the off-gas of an electric furnace used to produce ferrosilicon or silicon metal.

11. An aqueous slurry as claimed in any one of Claims 6 to 10 which includes one or more conventional additives in addition to said at least one ingredient in said slurry admixture.
12. A hardened concrete structural element which is formed of concrete batch materials to which has been added an admixture comprising a non-high-range water-reducing agent and/or a high-range water-reducing agent dispersed in microsilica in which the microsilica in the structural element is present in an amount from about 2% to about 100% of microsilica by weight based on the weight of cement in the structural element and the said at least one ingredient being present in said structural element an amount from about 0.1% to about 5.0% by weight based on the weight of cement in the structural element.

13. A hardened concrete structural element as claimed in Claim 12 which includes one or more non-high range water-reducing agents and one or more high-range water-reducing agents.

14. A hardened concrete structural element as claimed in Claim 12 or 13 in which the admixture added to the concrete includes one or more conventional concrete additives.

15. A process of forming a multicomponent admixture additive for concrete, which process comprises the steps of mixing a non-high-range water-reducing agent and/or a high-range water-reducing agent with microsilica in an amount to provide from about 30% to about 98% by weight of said admixture and adding from about 2.0% to about 50% by weight based on the weight of microsilica of the water-reducing agent in the admixture and continuing the mixing until the water-reducing agent is uniformly dispersed in the microsilica.
16. A process of forming a multicomponent admixture additive for cement, which process comprises the steps of mixing a non-high range water-reducing agent and/or a high-range water-reducing agent with water and with microsilica, adding the microsilica to the aqueous slurry in an amount to provide from 10% to 80% by weight of microsilica in the aqueous slurry and adding the water reducing agent in an amount to provide from 0.5% to 40% by weight (dry weight) of the water reducing agent in the aqueous slurry.

17. A process as claimed in Claim 15, which process includes the step of adding the admixture to a conventional concrete batch in an amount sufficient to provide from 2% to 100% by weight of the microsilica based on the weight of cement in the concrete and from 0.10% to 5.0% by weight of the water-reducing agent based on the weight of cement in the concrete batch.

18. A process of making a fresh concrete batch, which process comprises the steps of forming a multicomponent aqueous slurry admixture by combining and mixing a non-high range water-reducing agent and/or a high-range water-reducing agent with water and with microsilica adding the aqueous slurry admixture to a batch of fresh concrete in an amount sufficient to provide from 2% to about 100% by weight of microsilica based on the weight of cement in the concrete and from 0.10% to 5.0%
by weight of the water-reducing agent based on the weight of the cement and mixing the fresh concrete and aqueous slurry admixture to distribute the admixture ingredients therein.

5. A process as claimed in Claim 18, which process includes the step of adjusting the pH of the aqueous slurry admixture to from 3.0 to 7.5 during the mixing thereof.

10. A process as claimed in Claim 18 or 19, which includes the step of continuing to mix the aqueous slurry admixture ingredients until the microsilica and the water-reducing agent are uniformly and homogeneously dispersed in intimate contact therein.

15. A process as claimed in Claim 18, 19 or 20, which includes the step of adding and mixing one or more additional conventional additives into the aqueous slurry admixture.

20. A process as claimed in Claim 21, in which the/or one of the conventional additives is a retarder or air entraining agent.

22. A process as claimed in Claim 21, in which the/or one of the conventional additives is a retarder or air entraining agent.

25. An aqueous slurry comprising microsilica stabilized against gelation with a non-high range water-reducing agent and/or a high-range water reducing agent present in the slurry in an amount from 0.1% to 10% by weight (dry basis) based on the weight of microsilica in the slurry.
24. An aqueous slurry as claimed in Claim 23, which includes one or more high-range water-reducing agents and one or more non-high range water-reducing agents.

25. A process as claimed in Claim 16, which includes the step of adding one or more high-range water-reducing agents and one or more non-high range water reducing agents to the aqueous slurry.

26. A cement or mortar additive substantially as described herein.

27. An aqueous slurry substantially as described herein.

28. A hardened concrete structural element substantially as described herein.

29. A process of forming a multicomponent admixture additive for concrete substantially as described herein.

30. A process of making a fresh concrete batch substantially as described herein.

31. A cement or mortar additive comprising microsilica and a non-high range water reducing agent or a high-range water reducing agent.

Dated this 7th day of December, 1983.

ELKEM a/s,
By their Patent Attorneys,
COLLISON & CO.