

EUROPEAN QUALIFYING EXAMINATION 2003

PAPER B CHEMISTRY

This paper comprises:

- | | | |
|---|---|--------------------|
| * | Annex 1
Description of the Application | 2003/B(Ch)/e/1-9 |
| * | Annex 2
Communication | 2003/B(Ch)/e/10-11 |
| * | Annex 3
Document D1 | 2003/B(Ch)/e/12-16 |
| * | Annex 4
Document D2 | 2003/B(Ch)/e/17-22 |

Annex 1 (Application)

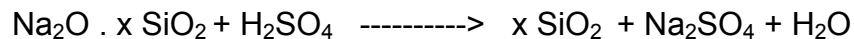
DESCRIPTION OF THE APPLICATION

The present invention relates to a precipitated silica which can be used as a reinforcing filler in rubber compositions, notably in the manufacture of treads for tyres.

5 The present invention further relates to a process for preparing the said precipitated silica.

It is well known to the skilled person that precipitated silica, chemical formula SiO_2 , may be obtained by reacting sodium silicate of the formula $\text{Na}_2\text{O} \cdot x \text{SiO}_2$ (where x is a number varying according to the chosen sodium silicate) with a mineral acid such as sulphuric acid in the following reaction sequence:

10



in which the resultant silica is precipitated. During precipitation, a three-dimensional network of silica is formed, resulting in the production of silica particles, which typically have a porous structure.

15

The skilled person also knows that the use of precipitated silica in rubber compositions, in particular in the manufacture of tyres, allows certain mechanical properties of the said compositions or tyres incorporating them to be enhanced. The precipitated silica has reinforcing properties, and is therefore also referred to as a reinforcing filler.

20

It would be desirable to have a precipitated silica which, when used in rubber compositions for tyres, gives the tyres low rolling resistance, good adherence to wet or snow-covered ground and high wear resistance.

25

Research conducted by the applicants has led to them finding such a precipitated silica. It takes the form of beads with high dispersibility and exceptional reinforcing properties.

The mean diameter of the silica beads according to the invention must be no more than 500 nm, in order to maintain sufficient reinforcing action. Below that value, any variation in the mean diameter has no impact on the reinforcing properties, particularly in relation to the manufacture of tyres.

5

The silica beads according to the invention have a BET specific surface area ranging from 50 to 500 m²/g, and preferably from 250 to 350 m²/g. The BET specific surface area is a common measurement parameter for the porosity of precipitated silica. The skilled person knows that the reinforcing action of a silica depends on its porosity and hence on this value.

10

The DOP oil absorption of the silica beads according to the present invention typically ranges from 180 to 450 ml/100 g and may vary from 300 to 400 ml/100 g. This value, which also depends on the structure of the silica, is also a common parameter, which is different from the BET specific surface area. It likewise characterises the reinforcing action of a silica and also indicates its dispersibility in rubber.

15

These precipitated silica beads may be obtained by the process below, to which the application also relates. It involves reacting an aqueous solution of one or more silicates with an acidifying agent, thereby producing a suspension of precipitated silica, then separating and drying that silica, characterised in that reaction is achieved in the following way:

20

- (i) an aqueous solution of one or more silicates containing the total amount of the silicate to be employed in the reaction is placed in a reactor, the silicate concentration in the reactor being less than 80 g/l expressed in g of SiO₂ per litre,
- (ii) the acidifying agent is added to the said reactor until the reaction medium has a pH value which is equal to 7 or less,
- (iii) the reaction is carried out with agitation leading to precipitation of the silica beads.

25

30

An essential feature of this process is that the initial silicate concentration in the reactor is less than 80 expressed in g of SiO₂ per litre. This concentration is preferably less than 70 g/l, and especially less than 60 g/l. This initial concentration has been found to constitute an important condition for giving the resultant silicas their excellent properties.

5

The silicate used may be any common form of water-soluble silicate such as, in particular, sodium or potassium silicate.

10

If sodium silicate is used, it typically has an SiO₂/Na₂O weight ratio of from 2 to 4:1, and more particularly from 3.0 to 3.7:1.

15

The second stage involves adding the acidifying agent to the reactor. The acidifying agent may be a strong mineral acid such as sulphuric acid, nitric acid or hydrochloric acid or an organic acid such as acetic acid, formic acid or carbonic acid. The addition of this agent lowers the pH of the reaction medium and is continued until its value is equal to 7 or less, which makes it possible to produce a silica with useful properties having a BET specific surface area ranging from 50 to 500 m²/g.

20

If, however, the desired silica is to have a preferred BET specific surface area ranging from 250 to 350 m²/g and a DOP oil absorption ranging from 300 to 400 ml/100 g, then the pH must not be lower than 5.0.

The temperature of the reaction medium typically ranges from 10 to 95°C.

25

The duration of the reaction is heavily dependent on the chosen pH range.

30

At a pH below 5.0, for example of the order of 4.0, the reaction is instantaneous, that is to say it immediately produces a silica whose properties, for example the BET specific surface area, no longer change. Such a rapid process, requiring little energy input, is particularly advantageous in industrial terms.

If the pH is greater than or equal to 5.0, the reaction proceeds slowly and the structure of the silica continues to change until the reaction is stopped. So in these pH conditions, to obtain a silica with a BET specific surface area ranging for example from 250 to 350 m²/g, the reaction has to be allowed to progress and then stopped when the desired silica is
5 obtained. For each pH value greater than or equal to 5.0 and as a function of the reaction temperature, the skilled person establishes on the basis of various routine tests what reaction time is needed to obtain the required silica. In this respect it should be noted that reaction speed increases with the temperature of the reaction medium. The resultant process makes it possible, under these pH conditions, to adjust the BET
10 specific surface area of the precipitated silica.

The above phenomena have not yet been entirely elucidated, but are clearly to be explained by the existence of different types of reaction mechanisms as a function of the
15 pH.

Following the operations described above, the precipitated silica is separated and then dried. The preferred drying technique is spray drying.

Although the BET specific surface area and the DOP oil absorption may vary
20 significantly depending on the conditions used for the precipitated silica preparation process, it should be noted that they are not independently adjustable parameters. These two parameters depend on the pH conditions used in preparing the precipitated silica. Thus the applicants have observed that for a pH value greater than or equal to 5.0 the choice of a BET specific surface area in the range from 250 to 350 m²/g inevitably
25 results in a DOP oil absorption in the range from 300 to 400 ml/100 g.

According to another aspect of the invention, the precipitated silica obtained according to the invention is used to reinforce rubber and in particular tyres, especially in the manufacture of tyre treads. In particular it gives such tyres good adherence to wet or
30 snow-covered ground, high wear resistance and low rolling resistance, which is good for fuel economy.

The invention is illustrated by the following examples.

Example 1

- 5 The following were placed in a stainless-steel reactor equipped with a propeller-type
agitating system and a double-jacketed heater:
- 772 litres of water
 - 211 litres of aqueous sodium silicate having an $\text{SiO}_2/\text{Na}_2\text{O}$ weight ratio of 3.45:1
- 10 and a density at 20°C of 1.230.

The silicate concentration in the reactor was then 50 g/l (expressed in g of SiO_2 per
litre). Dilute sulphuric acid having a density at 20°C of 1.050 was added to this mixture
until a pH value of 5.7 was attained in the reaction medium. The mixture was then
15 heated to a temperature of 50°C while being continuously agitated. The reaction was
stopped after 30 minutes. The precipitated silica was separated, washed and dried. The
product was a silica P1 in bead form having the properties indicated in Table I.

Examples 2 to 4

20

Example 1 was repeated under the pH, temperature and reaction duration conditions
indicated in Table I. In examples 3 and 4 the precipitated silica was obtained
immediately. The table also indicates the properties of the beads of silica P2 to P4 thus
obtained.

Table I

Silica	P1 (Example 1)	P2 (Example 2)	P3 (Example 3)	P4 (Example 4)
pH	5.7	5.3	4.0	3.0
T (°C)	50	40	20	20
Reaction duration	Stopped after 47 min	Stopped after 23 min	Silica obtained immediately	Silica obtained immediately
BET specific surface area (m ² /g)	270	330	180	280
DOP oil absorption (ml/100 g)	330	380	350	420
Mean diameter (nm)	< 500	< 500	< 500	< 500

Examples 5 to 8

The invention is illustrated by the following examples using the conventionally
manufactured 175/70 R13 radial-ply tyres identical in all respects other than the rubber
composition constituting the tread.

The compositions constituting the tested treads are indicated in Table II below. All the
elements of the composition are expressed in parts by weight per hundred parts of
rubber.

Table II

Composition	Example 5	Example 6	Example 7	Example 8
Rubber ⁽⁷⁾	100	100	100	100
Silica used	50 / P1 ⁽¹⁾	50 / P2 ⁽²⁾	50 / P3 ⁽³⁾	50 / P4 ⁽⁴⁾
Coupling agent ⁽⁵⁾	4	4	4	4
Stearic acid	1	1	1	1
Zinc oxide	2.5	2.5	2.5	2.5
Sulphur	1.4	1.4	1.4	1.4
Sulphenamide ⁽⁶⁾	1.7	1.7	1.7	1.7
Diphenylguanidine	1.5	1.5	1.5	1.5

(1) Silica P1 obtained as per example 1

(2) Silica P2 obtained as per example 2

(3) Silica P3 obtained as per example 3

(4) Silica P4 obtained as per example 4

(5) Bis(3-triethoxysilylpropyl)-tetrasulphide

(6) Sulphenamide: N-cyclohexyl-2-benzothiazyl sulphenamide

(7) Superflex

The properties of the four tyres according to the invention equipped with a tread made from a composition according to the invention comprising one of the silicas P1 to P4 (compositions of examples 5 to 8) were evaluated and are shown in Table III below as a function of the silica used.

Table III

Tyre properties	Example 5 (silica P1)	Example 6 (silica P2)	Example 7 (silica P3)	Example 8 (silica P4)
Adherence to wet ground	102	102	103	100
Adherence to snow-covered ground	121	120	104	100
Rolling resistance	105	103	104	105
Wear resistance	102	100	100	101

Adherence to wet ground: determination of the behaviour and performance of tyres running on a wetted track comprising various road surfacing compositions and exhibiting straight lines and curves. The higher the number, the better the adherence.

- 5 Adherence to snow-covered ground: determination of the behaviour and performance of tyres in various snowy conditions encountered in winter road traffic. The higher the number, the better the adherence.

Rolling resistance: the higher the value, the lower the rolling resistance.

10

Wear resistance: determined by the kilometres covered before the wear reaches the wear indicators placed in the grooves. The higher the number, the greater the wear resistance.

- 15 The rubber composition according to the invention is found to give a tyre tread not only very low rolling resistance and good adherence to wet or snow-covered ground but also high resistance to wear.

Claims

1. Precipitated silica in the form of beads with a mean diameter which is less than or equal to 500 nm and a BET specific surface area ranging from 50 to 500 m²/g.
2. Process for preparing beads of precipitated silica, involving reacting an aqueous solution of one or more silicates with an acidifying agent to produce a precipitated silica suspension, then separating and drying this silica, characterised in that the reaction is achieved as follows:
 - (i) an aqueous solution of one or more silicates containing the total amount of the silicate to be employed in the reaction is placed in a reactor, the silicate concentration in the said reactor being less than 80 g/l expressed in g of SiO₂ per litre;
 - (ii) the acidifying agent is added to the said reactor until the reaction medium has a pH value which is equal to 7 or less;
 - (iii) the reaction is carried out with agitation leading to precipitation of the silica beads.
3. Rubber composition comprising a silica according to claim 1.
4. Tyre comprising the composition according to claim 3.

Annex 2 (COMMUNICATION)

1. Document D1 in examples 1 and 2 discloses silicas S1 and S2, which meet the conditions set out in claim 1 of the present application. These silicas may be used to reinforce rubber, particularly in the manufacture of tyres (see D1, page 2, 1st paragraph). Thus the subject-matter of claims 1, 3 and 4 is disclosed by D1.

Moreover, claim 1 and examples 1 and 2 in D1 describe the process according to claim 2 of the present application.

The subject-matter of claims 1, 3 and 4 of the application is also anticipated by document D2, which describes silica beads having a BET specific surface area of 150 m²/g and a mean particle diameter of 450 nm (example 2) and a BET surface area of 300 m²/g and a mean particle diameter of 480 nm (example 3), and their use in rubber-based compositions for the manufacture of tyres.

Hence the subject-matter of claims 1 to 4 is not new within the meaning of Article 54 EPC.

2. If the applicants wish to maintain the application, they must file new claims meeting the requirements of the EPC, in particular Articles 54, 56, 82, 84 and 123(2) and Rule 29(2) EPC.

To simplify examination of this new set of claims, the applicants are invited to indicate exactly how the new claims can be derived from the documents of the application as filed (Article 123(2) EPC, Guidelines E-II, 1 and C-VI, 5.4).

The applicants must also indicate how the lack-of-novelty objection set out above has been overcome. They should use the problem/solution approach to explain why the subject-matter of the amended claims involves an inventive step within the meaning of Article 56 EPC.

In keeping with the Guidelines (C-III, 4.4), an independent claim must specify all the essential features, which means that each independent claim must indicate all the features needed to solve the problem underlying the invention.

Annex 3 (DOCUMENT D1)

The present invention relates to a novel process for preparing precipitated silica, to the precipitated silicas obtainable by this process and to their use as reinforcing fillers in rubber compositions.

- 5 It is known that precipitated silica has long been used as a reinforcing filler in rubber compositions, and particularly in tyres.

Like any reinforcing filler, however, it must be readily handleable and easy to incorporate into mixtures.

10

In this respect, silica in the powder form is not always satisfactory in that, purely from the standpoint of handling and use, it may entail considerable dust formation and slow incorporation of the filler; furthermore, rubber mixing requires very accurate metering techniques, for which powdery fillers are often unsuitable because they are difficult to
15 pour.

Another difficulty resides in the fact that silica particles have an unfortunate tendency to agglomerate within the rubber matrix. These silica/silica interactions have the deleterious effect of limiting the reinforcing properties to a level well below that which
20 could theoretically be attained.

Moreover, such silica/silica interactions tend to increase the viscosity of the mixtures, thus rendering them more difficult to use.

- 25 The aim of the present invention is to provide a novel process for preparing precipitated silica having greater dispersibility and better reinforcing properties than prior-art silicas.

The invention also relates to the precipitated silicas obtainable by this process. These take the form of beads having greater dispersibility and better reinforcing properties.

It also relates to the use of the said precipitated silicas as reinforcing fillers for rubber compositions, notably for tyres.

Thus one of the objects of the invention is a process for preparing beads of precipitated silica having improved dispersibility and reinforcing properties, of a type which involves reacting an aqueous solution of one or more silicates with an acidifying agent, thereby producing a suspension of precipitated silica, then separating and drying this silica, characterised in that the reaction is achieved as follows:

- (i) an aqueous solution of one or more silicates containing the total amount of the silicate to be employed in the reaction is placed in a reactor, the silicate concentration in the said reactor being less than 80 g/l expressed in g of SiO_2 per litre;
- (ii) the acidifying agent is added to the said reactor until the reaction medium has a pH value which equal is to 7 or less;
- (iii) the reaction is carried out with agitation leading to precipitation of the silica beads.

A low silicate concentration in the reactor is an essential initial condition for giving the resultant products their excellent properties. The initial silicate concentration in the reactor is less than 80 expressed in g of SiO_2 per litre. This concentration is preferably less than 70 g/l, and notably less than 55 g/l. The initial silicate concentration in the reactor partly determines the porosity of the resultant silicas.

The silicate used may be any common form of water-soluble silicate such as the metasilicates, disilicates and, advantageously, an alkali metal silicate, particularly sodium or potassium silicate.

If sodium silicate is used, it typically has an $\text{SiO}_2/\text{Na}_2\text{O}$ weight ratio of from 2 to 4:1, and more particularly from 3.0 to 3.7:1.

The second stage involves adding the acidifying agent to the reactor. The addition of this agent lowers the pH of the reaction medium and is continued until its value is 7 or less.

The acidifying agent may be a strong mineral acid such as sulphuric acid, nitric acid or
5 hydrochloric acid or an organic acid such as acetic acid, formic acid or carbonic acid.

The temperature of the reaction medium typically ranges from 10 to 95°C.

The product of the steps described above is a precipitated silica which is then separated
10 and dried. The preferred drying technique is spray drying.

The precipitated silica obtainable according to the invention takes the form of beads
having a mean diameter which is less than or equal to 500 nm. They generate little dust
and exhibit good pourability, very high dispersibility and excellent reinforcing properties.
15 These properties make them particularly suitable for rubber reinforcement and notably
for the manufacture of tyre treads.

The invention is illustrated by examples 1 and 2 below.

Example 1

5

The following were placed at a temperature of 20°C in a stainless-steel reactor equipped with a propeller-type agitating system and a double-jacketed heater:

- 772 litres of water
- 10 - 211 litres of aqueous sodium silicate having an $\text{SiO}_2/\text{Na}_2\text{O}$ weight ratio of 3.45:1 and a density at 20°C of 1.230.

The silicate concentration in the reactor was then 50 g/l (expressed in g of SiO_2 per litre). Dilute sulphuric acid having a density at 20°C of 1.050 was added to this mixture
15 until a pH value of 3.0 was attained in the reaction medium. The silica was obtained immediately. The precipitated silica was separated, washed and dried. The resultant silica S1 took the form of beads having a BET specific surface area of 280 m^2/g and a mean diameter of less than 500 nm.

20

Example 2

Example 1 was repeated in exactly the same form but using a pH of 4.0. A silica S2 was likewise obtained immediately. The silica S2 took the form of beads having a BET
25 specific surface area of 180 m^2/g and a mean diameter of less than 500 nm.

Claims

1. Process for preparing beads of precipitated silica, involving reacting an aqueous solution of one or more silicates with an acidifying agent to produce a precipitated silica suspension, then separating and drying this silica, characterised in that the reaction is achieved as follows:
 - (i) an aqueous solution of one or more silicates containing the total amount of the silicate to be employed in the reaction is placed in a reactor, the silicate concentration in the said reactor being less than 80 g/l expressed in g of SiO₂ per litre;
 - (ii) the acidifying agent is added to the said reactor until the reaction medium has a pH value which is equal to 7 or less;
 - (iii) the reaction is carried out with agitation leading to precipitation of the silica beads.
2. Precipitated silica in bead form obtainable by the process defined in claim 1.
3. Rubber composition comprising a silica according to claim 2.

Annex 4 (DOCUMENT D2)

The present invention relates to a rubber composition, comprising silica or alumina as a reinforcing filler, which can be employed in the manufacture of tyre treads.

5 Many solutions have been proposed for lowering the rolling resistance and improving the adherence of tyres, but they generally entail a very considerable loss of wear resistance. Indeed, the skilled person is well aware that the incorporation of conventional fillers such as silica or alumina into rubber compositions used in the manufacture of tyres, and especially of treads, undoubtedly entails a lowering of the rolling resistance and improved adherence to wet, snow-covered or icy ground, but also an unacceptable wear
10 resistance.

Surprisingly and unexpectedly it has been discovered that the use of a silica or alumina as defined in claim 1 may make it possible to obtain a rubber composition which can be employed in the manufacture of tyres and which exhibits advantageous properties such
15 as very low rolling resistance, improved adherence to dry and to wet or snow-covered ground, and also very good resistance to wear.

The subject of the present invention is a rubber composition comprising, as a reinforcing filler, alumina or silica beads having a BET specific surface area ranging from 25 to
20 400 m²/g, and preferably from 80 to 250 m²/g.

Alumina or silica beads in accordance with the invention may be used in a proportion of 20 to 300 parts by weight, and preferably 40 to 250 parts by weight, per hundred parts by weight of rubber.

If the mean diameter of the alumina or silica particles is greater than 500 nm, the reinforcing action of the alumina or silica according to the invention tends to diminish. Below that value, any variation in the mean diameter has no impact on the properties of the tyre. Consequently, the mean bead diameter is preferably less than or equal to
5 500 nm.

The rubber composition according to the invention gives a tyre tread not only the usual properties of silica or alumina, ie low rolling resistance and improved adherence to dry, wet or snow-covered ground, but also higher wear resistance than is provided by
10 mixtures containing carbon black.

The rubbers suitable for use in the composition according to the invention are natural rubber and synthetic rubbers such as Superflex or Hyperflex.

15 The composition according to the invention also contains the other constituents and additives usually employed in rubber mixes, such as plastifiers, antioxidants, sulphur, vulcanisation accelerators, or a reinforcing agent such as a silane.

Examples

The invention is illustrated by the following examples and a reference example using conventionally manufactured 175/70 R13 radial-ply tyres identical in all respects other
5 than the rubber composition constituting the tread.

The tested compositions constituting the treads are indicated in the table below. All the components of the composition are expressed in parts by weight per hundred parts of rubber.

Composition	Example 1	Example 2	Example 3	Reference example
Rubber ⁽⁶⁾	100	100	100	100
Alumina ⁽¹⁾	90	-	-	-
Silica ⁽²⁾	-	70	-	-
Silica ⁽³⁾	-	-	70	-
Carbon black	-	-	-	70
Coupling agent ⁽⁴⁾	6	6	6	-
Stearic acid	1	1	1	1
Zinc oxide	2.5	2.5	2.5	2.5
Sulphur	2.1	2.1	2.1	2.1
Sulphenamide ⁽⁵⁾	1.7	1.7	1.7	1.7
Diphenylguanidine	1.5	1.5	1.5	1.5

- (1) Alumina having a BET specific surface area of $200 \text{ m}^2/\text{g}$, a mean particle diameter of 380 nm and a DOP oil absorption of 450 ml/100 g.
- (2) Silica in the form of beads having a BET specific surface area of $150 \text{ m}^2/\text{g}$, a DOP oil absorption of 350 ml/100 g and a mean diameter of 450 nm.
- (3) Silica in the form of beads having a BET specific surface area of $300 \text{ m}^2/\text{g}$, a DOP oil absorption of 520 ml/100 g and a mean diameter of 480 nm.
- (4) Bis(3-triethoxysilylpropyl)-tetrasulphide
- (5) Sulphenamide: N-cyclohexyl-2-benzothiazyl sulphenamide
- (6) Hyperflex

The three tyres equipped with a tread made from a composition according to the invention (compositions of examples 1 to 3) were compared with a tyre equipped with a tread according to the prior art (composition of the reference example).

- 5 The properties of adherence to snow-covered or wet ground, rolling resistance and wear resistance were evaluated for the compositions of examples 1 to 3 and the composition of the reference example.

10 Adherence to wet ground: determination of the behaviour and performance of tyres running on a wetted track comprising various road surfacing compositions and exhibiting straight lines and curves. The higher the number, the better the adherence.

15 Adherence to snow-covered ground: determination of the behaviour and performance of tyres in various snowy conditions encountered in winter road traffic. The higher the number, the better the adherence.

Rolling resistance: the higher the value, the lower the rolling resistance.

Wear resistance: determined by the kilometres covered before the wear reaches the wear indicators placed in the grooves. The higher the number, the greater the wear resistance.

Tyre properties	Composition as in example 1	Composition as in example 2	Composition as in example 3	Composition as in the reference example
Adherence to wet ground	102	102	103	100
Adherence to snow-covered ground	105	103	104	100
Rolling resistance	115	104	104	100
Wear resistance	102	101	100	94

The rubber composition according to the invention is found to give a tyre tread not only with a low rolling resistance and improved adherence to dry, wet or snow-covered ground but also higher wear resistance than is provided by mixtures containing carbon black.

Claims

1. Rubber composition comprising alumina or silica, characterised in that the alumina or silica is in bead form and has a BET specific surface area ranging from 25 to 400 m²/g.
2. Composition according to claim 1, characterised in that the alumina or silica is present in a proportion of 20 to 300 parts by weight per 100 parts by weight of rubber.
3. Composition according to either of claims 1 or 2, characterised in that the BET specific surface area of the alumina or silica beads ranges from 80 to 250 m²/g.
4. Composition according to any of claims 1 to 3, characterised in that the mean diameter of the alumina or silica particles is equal to or less than 500 nm.
5. Tyre characterised in that it comprises a rubber composition as defined in claims 1 to 4.