Innovation, Sciences et Développement économique Canada
Office de la Propriété Intellectuelle du Canada

Innovation, Science and Economic Development Canada
Canadian Intellectual Property Office

CA 3238552 A1 2023/06/29

(21) **3 238 552**

(12) DEMANDE DE BREVET CANADIEN CANADIAN PATENT APPLICATION

(13) **A1**

(86) **Date de dépôt PCT/PCT Filing Date:** 2022/12/21
(87) **Date publication PCT/PCT Publication Date:** 2023/06/29
(85) **Entrée phase nationale/National Entry:** 2024/05/17
(86) **N° demande PCT/PCT Application No.:** EP 2022/087217
(87) **N° publication PCT/PCT Publication No.:** 2023/118286
(30) **Priorité/Priority:** 2021/12/23 (EP21306930.5)

(51) **Cl.Int./Int.Cl.** ***C01B 33/193*** (2006.01), ***C01B 33/12*** (2006.01), ***C01B 33/143*** (2006.01), ***C09C 1/30*** (2006.01)

(71) **Demandeur/Applicant:**
COMPAGNIE GENERALE DES ETABLISSEMENTS MICHELIN, FR

(72) **Inventeurs/Inventors:**
FERAL-MARTIN, CEDRIC, FR;
ALLAIN NAJMAN, EMMANUELLE, FR;
LAURIOL-GARBEY, PASCALINE, FR;
CHAUSSEE, THOMAS, FR;
GUY, LAURENT, FR; ...
BADOIL, LAURENT, FR;

(54) **Titre : COMPOSITIONS ELASTOMERES DE PNEU COMPRENANT UNE SILICE PRECIPITEE**
(54) **Title: TIRE ELASTOMERIC COMPOSITIONS COMPRISING A PRECIPITATED SILICA**

(57) **Abrégé/Abstract:**
The present invention relates to tire elastomeric compositions comprising at least a specific precipitated silica having an improved dispersibility. The invention further relates to semi-finished articles for tire and to tires comprising such tire elastomeric compositions.

(72) **Inventeurs(suite)/Inventors(continued):** PIFFARD, OLIVIER, FR

(74) **Agent:** ROBIC AGENCE PI S.E.C./ROBIC IP AGENCY LP

Date Submitted: 2024/05/17

CA App. No.: 3238552

Abstract:

The present invention relates to tire elastomeric compositions comprising at least a specific precipitated silica having an improved dispersibility. The invention further relates to semi-finished articles for tire and to tires comprising such tire elastomeric compositions.

Description

TIRE ELASTOMERIC COMPOSITIONS COMPRISING A PRECIPITATED SILICA

Technical Field

The present invention relates to reinforced elastomeric compositions being especially intended for the manufacture of tyres or of semi-finished products for tyres, in particular for treads of these tyres.

Background Art

The use of precipitated silica as a reinforcing filler in polymeric compositions is known. In particular it is known to use precipitated silica as reinforcing filler in elastomeric compositions. Such use is highly demanding: the filler has to readily and efficiently incorporate and disperse in the elastomeric composition and, typically in conjunction with a coupling agent, enter into a chemical bond with the elastomer(s), to lead to a high and homogeneous reinforcement of the elastomeric composition. In general, precipitated silica is used in order to improve the mechanical properties of the elastomeric composition as well as handling and abrasion performance.

WO 03/016215 discloses a precipitated silica having given properties namely in terms of granulometry (measured by XDC or X-ray Disc Centrifuge) and porosity of the primary particles aggregates. Although this silica performs very well as reinforcement for elastomeric compositions, the Applicant has now found that in order to improve the dispersibility of such a precipitated silica in polymeric compositions (which in turn improves their wear resistance), it is advantageous to have inhomogeneous aggregates showing a core/shell structure with a friable core.

Summary of invention

It has been found that a good dispersion in tire elastomeric compositions can be obtained with a specific precipitated silica.

One object of the present invention is a tire elastomeric composition based on at least one elastomer, at least one reinforcing filler comprising at least one precipitated silica, at least one coupling agent between the elastomer and the precipitated silica and at least one crosslinking system, said precipitated silica being characterised by:

- a CTAB surface area in the range from 40 to 525 m^2/g,
- primary particles having an average size measured by SAXS below 15 nm,
- an amount of aluminium W_{Al} of at least 0.50 wt%,
- a proportion (by weight) of particles of a size less than 1 μm after deagglomeration by ultrasounds, which is of at least 91%; and
- a particle size distribution measured by centrifugal sedimentation using a CPS, such that for a given value of the CTAB surface area, parameter FWHM is defined by relation (I):

  $$| FWHM | > -0.16 \times | CTAB | + 130 \qquad (I).$$

Additionally, it has been surprisingly found that the use of said specific precipitated silica as described above lead to obtain tire elastomeric compositions having a good compromise of mechanical properties. Advantageously, the tire elastomeric compositions of the invention have improved grip on wet ground properties.

Description of invention

In the present specification, the terms "silica" and "precipitated silica" are used as synonyms.

In the present specification numerical ranges defined by the expression "between a and b" indicate a numerical range which excludes end values a and b. Numerical ranges defined by the expression "from a to b" indicate a numerical range which includes end values a and b.

The term "below" is used herein under its usual, commonly accepted meaning, that is "less than a particular amount or level", as it can be notably found in Cambridge's Dictionary (online version available at https://dictionary.cambridge.org/dictionary/english/below"); likewise, the term "lower" is also used herein under its usual, commonly accepted meaning, that is "positioned below", as it can be found notably in Cambridge's Dictionary, so the terms "below" and "lower than", as used herein, have the same meaning, which is their usual, commonly accepted meaning".

Numerical ranges defined by the expression "a is at least b" indicate ranges wherein a is equal to or greater than b.

For the avoidance of doubts, the symbol "×" in relation (I) represents the multiplication sign, such that the expression "a×b" means a multiplied by b.

In relation, such as for example in relation (I), |CTAB| represents the numerical value of the CTAB surface area expressed in m^2/g. |CTAB| is an adimensional number. As an example, if the measured value of the CTAB is 200 m^2/g, |CTAB| is 200.

The same applies to the other values between | | below, which are all the adimensional numerical value of the parameter between said vertical bars.

The phrase "at least one" when referring to the ingredient in the composition is used herein to indicate that one or more than one ingredient of each type can be present in the composition.

The expression "copolymer" is used herein to refer to polymers comprising recurring units deriving from at least two monomeric units of different nature.

The expression composition "based on" should be understood as meaning a composition comprising the mixture and/or the reaction product of the various constituents used, some of these base constituents being capable of reacting, or intended to react, with one another, at least in part, during the various phases of manufacture of the composition, in particular during the crosslinking or vulcanization thereof.

In the present description, unless expressly indicated otherwise, all the percentages (%) shown are percentages by weight.

The abbreviation "phr" (per hundred parts of rubber) means parts by weight per hundred parts by weight of elastomers (of the total of the elastomers, if several elastomers are present) or rubber present in the elastomeric composition.

When reference is made to a "predominant" compound, it is understood, within the meaning of the present invention, that this compound is predominant among the compounds of the same type in the composition, that is to say that it is the one which represents the largest amount by mass among the compounds of the same type. Thus, for example, a predominant elastomer is the elastomer representing the greatest mass relative to the total mass of the elastomers in the composition. In the same way, a so-called majority filler is that representing the greatest mass among the fillers of the composition. By way of example, in a system comprising a single elastomer, the latter is predominant within the meaning of the present invention; and in a system comprising two elastomers, the predominant elastomer represents more than half the mass of the elastomers. Preferably, the term "predominant" is understood to mean present at more than 50%, preferably more than 60%, 70%, 80% and 90%, and more preferably the "predominant" compound represents 100%

The compounds mentioned in the description can be of fossil origin or biosourced. In the latter case, they may be partially or totally derived from biomass or obtained from renewable raw materials derived from biomass. In the same way, the compounds mentioned can also come from the recycling of materials already used, that is to say that they can be, partially or totally, from a recycling process, or obtained from materials raw materials themselves from a recycling process. This concerns in particular polymers, plasticizers, fillers, etc.

As said above, the tire elastomeric compositions of the present invention comprise at least one elastomer. Preferably, the elastomer exhibits at least one glass transition temperature Tg between -150°C and +300°C, for example between -150°C and +20°C. The glass transition temperature Tg of the elastomer is measured according to ASTM D3418, 2008.

Notable non-limiting examples of suitable elastomers are diene elastomers. Preferably, the elastomer of the tire elastomeric compositions of the invention is a dienic elastomer (or diene elastomer). More preferentially, the elastomer is a synthetic diene elastomer.

It is recalled here that elastomer (or "rubber", the two terms being regarded as synonymous) of the "diene" type should be understood, in a known way, as meaning an (one or more is understood) elastomer resulting at least in part (i.e., a homopolymer or a copolymer) from diene monomer(s) (i.e. monomer(s) bearing two conjugated or non-conjugated carbon-carbon double bonds).

More preferably diene elastomer capable of being used in the tire elastomeric compositions in accordance with the invention is intended more particularly to mean:

(a)any homopolymer obtained by polymerization of a conjugated diene monomer having from 4 to 12 carbon atoms.

(b)any copolymer obtained by copolymerization of one or more conjugated dienes with one another or with one or more vinylaromatic compounds having from 8 to 20 carbon atoms,

(c)a ternary copolymer obtained by copolymerization of ethylene and of an α-olefin having from 3 to 6 carbon atoms with a non-conjugated diene monomer having from 6 to 12 carbon atoms, such as, for example, the elastomers obtained from ethylene and propylene with a non-conjugated diene monomer of the abovementioned type, such as, especially, 1,4-hexadiene, ethylidene norbornene or dicyclopentadiene, (d)a copolymer of isobutene and of isoprene (butyl rubber) and also the halogenated versions, in particular chlorinated or brominated versions, of this type of copolymer.

Although it applies to any type of elastomer, especially diene elastomer, those skilled in the art will understand that the present invention is preferably employed with essentially unsaturated diene elastomers, in particular of the above type (a) or (b).

In the case of copolymers (b), the latter may contain from 20% to 99% by weight of diene units and from 1% to 80% by weight of vinylaromatic units.

As conjugated dienes, the following are especially suitable: 1,3-butadiene, 2-methyl-1,3-butadiene, 2,3-di(C1-C5 alkyl)-1,3-butadienes such as, for example, 2,3-dimethyl-1,3-butadiene, 2,3-diethyl-1,3-butadiene, 2-methyl-3-ethyl-1,3-butadiene, 2-methyl-3-isopropyl-1,3-butadiene, an aryl-1,3-butadiene, 1,3-pentadiene, or 2,4-hexadiene.

The following, for example, are suitable as vinylaromatic compounds: styrene, ortho-, meta- or para-methylstyrene, the “vinyltoluene” commercial mixture, para-(tert-butyl)styrene, methoxystyrenes, chlorostyrenes, vinylmesitylene, divinylbenzene or vinylnaphthalene.

For example, use may be made of elastomers deriving from aliphatic or aromatic monomers, comprising at least one unsaturation such as, in particular, ethylene, propylene, butadiene, isoprene, styrene, acrylonitrile, isobutylene or vinyl acetate, polybutyl acrylate, or their mixtures. Mention may also be made of functionalized elastomers, that is elastomers functionalized by chemical groups positioned along the macromolecular chain and/or at one or more of its ends (for example by functional groups capable of reacting with the surface of the silica), and halogenated polymers. Mention may be made of polyamides, ethylene homo- and copolymer, propylene homo-and copolymer. Other suitable elastomers are those including chloro- or bromo- butyl monomers (like bromo-butylene for instance).

Preferably, the elastomer of the tire elastomeric compositions of the invention is selected in the group consisting of polybutadienes, natural rubber, synthetic polyisoprenes, butadiene copolymers, isoprene copolymers and their mixtures.

Among diene elastomers mention may be made, for example, of polybutadienes (BRs), polyisoprenes (IRs) including natural rubber, butadiene copolymers, isoprene copolymers, or their mixtures, and in particular styrene/butadiene copolymers (SBRs, in particular ESBRs (emulsion) or SSBRs (solution)), isoprene/butadiene copolymers (BIRs), isoprene/styrene copolymers (SIRs), isoprene/butadiene/styrene copolymers (SBIRs), ethylene/propylene/diene terpolymers (EPDMs), and also the associated functionalized polymers (exhibiting, for example, pendant polar or reactive groups or polar groups at the chain end, which can interact or react with the silica).

The elastomers may have any microstructure, which depends on the polymerization conditions used, especially on the presence or absence of a modifying and/or randomizing agent and on the amounts of modifying and/or randomizing agent employed. These elastomers may, for example, coupled and/or star-branched or else functionalized with a coupling and/or star-branching or functionalization agent. Preferably, the (dienic) elastomers are statistical polymers.

Preferentially, the elastomer is a functionalized diene elastomer.

Preferably, the functionalized diene elastomer is a functionalized butadiene/styrene copolymer.

“Functionalized diene elastomer” is intended to mean a synthetic diene elastomer that comprises at least one chemical group comprising one or more heteroatoms, such as, for example, a sulphur atom S, a nitrogen atom N, an oxygen atom O, a silicon atom Si, or a tin atom Sn. Within the context of the present description, this chemical group is also referred to as “function”. The two terms are used without distinction.

This chemical group may be located at the chain end, that is to say at one end of the linear main elastomer chain. It will then be said that the diene elastomer is functionalized “at the chain end”. It is generally an elastomer obtained by reaction of a living elastomer with a functionalization agent, that is to say any at least monofunctional molecule, the function being any type of chemical group known by those skilled in the art to react with a living chain end.

This chemical group may be located in the linear main elastomer chain. It will then be said that the diene elastomer is coupled or else functionalized “in the middle of the chain”, in contrast to the position "at the chain end", although the group is not located precisely at the middle of the elastomer chain. It is generally an elastomer obtained by reaction of two chains of the living elastomer with a coupling agent, that is to say any at least difunctional molecule, the function being any type of chemical group known by those skilled in the art to react with a living chain end.

This group may be central, to which n elastomer chains (n>2) are bonded, forming a star-branched structure of the elastomer. It will then be said that the diene elastomer is star-branched. It is generally an elastomer obtained by reaction of n chains of the living elastomer with a star-branching agent, that is to say any polyfunctional molecule, the function being any type of chemical group known by those skilled in the art to react with a living chain end.

Those skilled in the art will understand that a functionalization reaction with an agent comprising more than one function which is reactive with regard to the living elastomer results in a mixture of entities functionalized at the chain end and in the middle of the chain, constituting the linear chains of the functionalized diene elastomer, and also, if appropriate, star-branched entities. Depending on the operating conditions, mainly the molar ratio of the functionalization agent to the living chains, certain entities are predominant in the mixture.

Preferentially, the functionalized diene elastomer comprises at least one polar function comprising at least one oxygen atom.

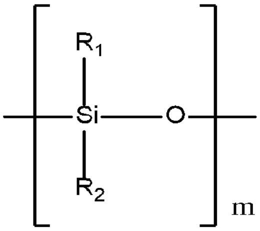
Preferentially, the polar function may be selected from the group consisting of silanol, alkoxysilanes, alkoxysilanes bearing an amine group, epoxide, ethers, esters, carboxylic acids and hydroxyl. The polar function especially improves the interaction between the reinforcing inorganic filler and the elastomer. Such functionalized elastomers are known per se and are described especially in the following documents: FR2740778, US6013718, WO2008/141702, FR2765882, WO01/92402, WO2004/09686, EP1127909, US6503973, WO2009/000750 and WO 2009/000752.

The functionalized diene elastomer is preferably a diene elastomer comprising a polar function that is a silanol.

Preferentially, the silanol is located at the chain end or in the middle of the chain of the main chain of the functionalized diene elastomer. More preferentially, the silanol is located at the chain end of the main chain of the functionalized diene elastomer.

Preferably, the functionalized diene elastomer is a diene elastomer, more preferably an SBR, in which the silanol function is located at the chain end. This functionalized diene elastomer comprises, at one end of the main chain thereof, a silanol function or a polysiloxane group having a silanol end of formula $-(SiR_1R_2\text{-}O-)_mH$ with m representing an integer with a value ranging from 3 to 8, preferably 3, R_1 and R_2, which are identical or different, represent an alkyl radical with 1 to 10 carbon atoms, preferably an alkyl radical having 1 to 4 carbon atoms.

This type of elastomer may be obtained according to the processes described in document EP0778311 and more particularly according to the process consisting, after a step of anionic polymerization, in functionalizing the living elastomer with a functionalization agent of cyclic polysiloxane type, as long as the reaction medium does not allow the polymerization of the cyclopolysiloxane. As cyclic polysiloxanes, mention may be made of those corresponding to formula (II):



(II)

where m represents an integer with a value ranging from 3 to 8, preferably 3, and R_1 and R_2, which are identical or different, represent an alkyl radical with 1 to 10 carbon atoms, preferably an alkyl radical having 1 to 4 carbon atoms. Mention may be made, among these compounds, of hexamethylcyclotrisiloxane.

More preferentially, the functionalized diene elastomer is a diene elastomer (especially an SBR) comprising, at one end of the main chain thereof, a silanol function or a polysiloxane group having a silanol end of formula $-(SiR_1R_2-O-)_mH$ with m representing an integer with a value equal to 3, preferably 3, R_1 and R_2, which are identical or different, represent an alkyl radical having 1 to 4 carbon atoms.

Preferentially, the functionalized diene elastomer, preferably the SBR, comprises a polar function which is an alkoxysilane bearing, or not bearing, another function (or bearing another chemical group, these expressions being synonymous).

Preferably, this functionalized diene elastomer comprises, within the main chain thereof, at least one alkoxysilane group bonded to the elastomer chain by the silicon atom, and optionally bearing at least one other function.

According to some variants, the alkoxysilane group (bearing or not bearing another function) is located at one end of the main chain of the elastomer (chain end).

According to other variants, the alkoxysilane group (bearing or not bearing another function) is located in the main elastomer chain (middle of the chain). The silicon atom of this function bonds the two branches of the main chain of the diene elastomer.

The alkoxysilane group (bearing or not bearing another function) comprises a C1-C10 alkoxyl radical, optionally partially or totally hydrolysed to give hydroxyl, or even a C1-C8, preferably C1-C4 alkoxyl radical, and is more preferentially methoxy and ethoxy.

The other function is preferably borne by the silicon of the alkoxysilane group, directly or via a spacer group, defined as being a saturated or unsaturated, cyclic or non-cyclic, divalent, linear or branched, aliphatic C1-C18 hydrocarbon-based radical or atom, or a divalent aromatic C6-C18 hydrocarbon-based radical.

The other function is preferably a function comprising at least one heteroatom chosen from N, S, O or P. Mention may be made, by way of example, among these functions, of cyclic or non-cyclic primary, secondary or tertiary amines, isocyanates, imines, cyanos, thiols, carboxylates, epoxides or primary, secondary or tertiary phosphines.

Mention may thus be made, as secondary or tertiary amine function, of amines substituted by C1-C10, preferably C1-C4, alkyl radicals, more preferentially a methyl or ethyl radical, or else cyclic amines forming a heterocycle containing a nitrogen atom and at least one carbon atom, preferably from 2 to 6 carbon atoms. For example, the methylamino-, dimethylamino-, ethylamino-, diethylamino-, propylamino-, dipropylamino-, butylamino-, dibutylamino-, pentylamino-, dipentylamino-, hexylamino-, dihexylamino- or hexamethyleneamino- groups, preferably the diethylamino- and dimethylamino- groups, are suitable.

Mention may be made, as imine function, of the ketimines. For example, the (1,3-dimethylbutylidene)amino-, (ethylidene)amino-, (1-methylpropylidene)amino-, (4-N,N-dimethylaminobenzylidene)amino-, (cyclohexylidene)amino-, dihydroimidazole and imidazole groups are suitable.

Mention may thus be made, as carboxylate function, of acrylates or methacrylates. Such a function is preferably a methacrylate.

Mention may be made, as epoxide function, of the epoxy or glycidyloxy groups.

Mention may be made, as secondary or tertiary phosphine function, of phosphines substituted by C1-C10, preferably C1-C4, alkyl radicals, more preferentially a methyl or ethyl radical, or else diphenylphosphine. For example, the methylphosphino-, dimethylphosphino-, ethylphosphino-, diethylphosphino, ethylmethylphosphino- and diphenylphosphino- groups are suitable.

Preferentially, the other function is preferably a tertiary amine, more preferentially a diethylamino- or dimethylamino- group.

Preferentially, the functionalized diene elastomer (especially an SBR) may comprise a polar function which is an alkoxysilane bearing, or not bearing, an amine group.

Preferentially, the alkoxysilane bearing, or not bearing, an amine group is located at the chain end or in the middle of the chain of the main chain of the functionalized diene elastomer. More preferentially, the alkoxysilane group bearing, or not bearing, the amine group is located in the middle of the chain of the main chain of the functionalized diene elastomer.

Preferentially, the amine group is a tertiary amine.

Preferably, the alkoxysilane group may be represented by the formula (III):

$$(*—)_a\mathrm{Si}\,(\mathrm{OR'})_b\mathrm{R}_c\mathrm{X} \qquad \text{(III)}$$

in which:

- *— represents the bond to an elastomer chain;
- the radical R represents a substituted or unsubstituted C1-C10, or even C1-C8 alkyl radical, preferably a C1-C4 alkyl radical, more preferentially methyl and ethyl;
- in the alkoxyl radical(s) of formula –OR', which is (are) optionally partially or totally hydrolysed to give hydroxyl, R' represents a substituted or unsubstituted C1-C10, or even C1-C8 alkyl radical, preferably a C1-C4 alkyl radical, more preferentially methyl and ethyl;
- X represents a group including the other function;
- a is 1 or 2, b is 1 or 2, and c is 0 or 1, with the proviso that a+b+c =3.

More preferentially, the functionalized diene elastomer is a diene elastomer (especially an SBR) that comprises, within the main chain thereof, at least one alkoxysilane group of formula (III), in which:

- *— represents the bond to an elastomer chain;
- the radical R represents a substituted or unsubstituted C1-C4 alkyl radical, more preferentially methyl and ethyl;

- in the alkoxyl radical(s) of formula –OR', which is (are) optionally partially or totally hydrolysed to give hydroxyl, R' represents a substituted or unsubstituted C1-C4 alkyl radical, more preferentially methyl and ethyl;
- X represents a group including the other function; preferably a tertiary amine;
- a is 1 or 2, b is 1 or 2, and c is 0 or 1, with the proviso that a+b+c =3.

This type of elastomer is mainly obtained by functionalization of a living elastomer resulting from an anionic polymerization. It should be specified that it is known to those skilled in the art that, when an elastomer is modified by reaction of a functionalization agent with the living elastomer resulting from a step of anionic polymerization, a mixture of modified entities of this elastomer is obtained, the composition of which depends on the modification reaction conditions and especially on the proportion of reactive sites of the functionalization agent relative to the number of living elastomer chains. This mixture comprises entities which are functionalized at the chain end, coupled, star-branched and/or non-functionalized.

According to a particularly preferred variant, the modified diene elastomer comprises, as predominant entity, the diene elastomer functionalized in the middle of the chain by an alkoxysilane group bonded to the two branches of the diene elastomer via the silicon atom. More particularly still, the diene elastomer functionalized in the middle of the chain by an alkoxysilane group represents at least 55% by weight of the modified diene elastomer.

These functionalized elastomers can be used as a blend (mixture) with one another or with non-functionalized elastomers.

The tire elastomeric compositions of the invention may comprise at least one polymer different from the elastomer or different form the dienic elastomer, said polymer may be selected among the thermosetting polymers and the thermoplastic polymers, the latter being preferred.

Notable, non-limiting examples of suitable thermoplastic polymers include styrene-based polymers such as polystyrene, (meth)acrylic acid ester/styrene copolymers, acrylonitrile/styrene copolymers, styrene/maleic anhydride copolymers, ABS; acrylic polymers such as polymethylmethacrylate; polycarbonates; polyamides; polyesters, such as polyethylene terephthalate and polybutylene terephthalate; polyphenylene ethers; polysulfones; polyaryletherketones; polyphenylene sulfides; thermoplastic polyurethanes; polyolefins such as polyethylene, polypropylene, polybutene, poly-4-methylpentene, ethylene/propylene copolymers, ethylene/ α-olefins copolymers; copolymers of α-olefins and various monomers, such as ethylene/vinyl acetate copolymers, ethylene/(meth)acrylic acid ester copolymers, ethylene/maleic anhydride copolymers, ethylene/acrylic acid copolymers; aliphatic polyesters such as polylactic acid, polycaprolactone, and aliphatic glycol/aliphatic dicarboxylic acid copolymers.

According to a specific embodiment, the content of the (dienic) elastomer in the tire elastomeric composition is more than 50 phr (that is to say from 50 to 100 phr), more preferably at least 60 phr (that is to say from 60 to 100 phr), more preferably at least 70 phr (that is to say from 70 to 100 phr), even more preferably at least 80 phr (that is to say from 80 to 100 phr) and very preferably at least 90 phr (that is to say from 90 to 100 phr).

When the tire elastomeric composition comprises a polymer other than the (dienic) elastomer, then the content of this polymer is less than 50 phr (that is to say from 0 to 50 phr), more preferably less than 40 phr (that is to say from 0 to 40 phr), more preferably less than 30 phr (that is to say from 0 to 30 phr), even more preferably less than 20 phr (that is to say from 0 to 20 phr) and very preferably less than 10 phr (that is to say from 0 to 90 phr).

As said above, the tire elastomeric composition comprises at least one reinforcing filler comprising at least one precipitated silica having by:

- a CTAB surface area in the range from 40 to 525 m^2/g;
- primary particles having an average size measured by SAXS below 15 nm;
- an amount of aluminium W_{Al} of at least 0.50wt%,
- a proportion (by weight) of particles of a size less than 1 μm after deagglomeration by ultrasounds, which is of at least 91%; and
- a particle size distribution measured by centrifugal sedimentation using a CPS, such that for a given value of the CTAB surface area, parameter FWHM is defined by relation (I):

  $$|\text{FWHM}| > -0.16 \times |\text{CTAB}| + 130 \qquad \text{(I)}.$$

The CTAB surface area is a measure of the external specific surface area as determined by measuring the quantity of N hexadecyl-N,N,N-trimethylammonium bromide adsorbed on the silica surface at a given pH.

The CTAB surface area is at least 40 m^2/g, typically at least 60 m^2/g. The CTAB surface area may be greater than 70 m^2/g. The CTAB surface area may even be greater than 110 m^2/g, greater than 120 m^2/g, greater than 130 m^2/g possibly even greater than 150 m^2/g.

The CTAB surface area does not exceed 525 m^2/g, typically not 300 m^2/g. The CTAB surface area may be lower than 280 m^2/g, lower than 250 m^2/g, lower than 230 m^2/g, possibly even lower than 210 m^2/g, lower than 190 m^2/g, lower than 180 m^2/g or lower than 170 m^2/g.

Especially for elastomer reinforcement applications advantageous ranges for the CTAB surface area are: from 50 to 300 m^2/g, preferably from 70 to 300 m^2/g, more preferably from 80 to 270 m^2/g or alternatively, from 120 to 275 m^2/g. Good results were notably obtained when the CTAB surface area was greater than 70 m^2/g and lower than 250 m^2/g, in particular when the CTAB surface area was greater than 120 m^2/g and lower than 230 m^2/g, more particularly when the CTAB surface area was greater than 120 m^2/g and lower than 180 m^2/g.

The BET surface area of the inventive silica used in the tire elastomeric compositions of the invention is not particularly limited but it is preferably at least 10 m^2/g higher than the CTAB surface area. The BET surface area is generally at least 80 m^2/g, at least 100 m^2/g, at least 120 m^2/g at least 140 m^2/g, at least 160 m^2/g, at least 170 m^2/g, at least 180 m^2/g, and even at least 200 m^2/g. The BET surface area may be as high as 300 m^2/g, even as high as 350 m^2/g; the BET surface may also be of at most 260 m^2/g, at most 240 m^2/g, at most 220 m^2/g, possibly even at most 200 m^2/g, at most 180 m^2/g or at most 170 m^2/g. In many embodiments, the BET surface area ranged from 100 m^2/g to 300 m^2/g.

The difference between the BET surface area and the CTAB surface area is generally taken as representative of the microporosity of the precipitated silica in that it provides a measure of the pores of the silica which are accessible to nitrogen molecules but not to larger molecules, like N hexadecyl-N,N,N-trimethylammonium bromide.

The precipitated silica used in the elastomeric compositions of the invention may be defined by a difference between the BET surface area and the CTAB surface area of at least 5 m^2/g, preferably at least 10 m^2/g. This difference is preferably not more than 40 m^2/g, preferably not more than 35 m^2/g.

The inventive silica used in the tire elastomeric compositions of the invention contains aluminium in an amount W_{Al} of at least 0.50wt% and typically of at most 3.00 wt%. Certain other suitable aluminium ranges W_{Al} are from 0.50 wt% to 1.50 wt% (in particular, from

0.50 wt% to 1.00 wt%), and from more than 1.50 wt% up to 3.00 wt%. Throughout the present text the amount of aluminium, W_{Al}, is defined as the percentage amount by weight of aluminium, meant as aluminium metal, with respect to the weight of SiO_2. The amount of aluminium is preferably measured using XRF wavelength dispersive X-ray fluorescence spectrometry. This aluminium is generally at least in part coming from the raw materials. In some embodiments, an aluminium compound (like sodium aluminate) is added during the synthesis of the precipitated silica and/or during the liquefaction step as described below.

It has to be understood that the inventive silica used in the tire elastomeric compositions of the invention may contain elements of which non-limiting examples are for instance Ga, B, Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Fe, Co, Mg, Ca or Zn. Hence, in one embodiment, the silica used in the tire elastomeric compositions of the invention contain at least one element selected from Ga, B, Sc, Y, Ti, Zr, Hf, V, Nb, Ta, Fe, Co, Mg, Ca or Zn.

The precipitated silica that are used in the tire elastomeric compositions of the invention is further characterised by a broad particle size distribution and by small sized primary particles. The term particle is used to refer to the smallest aggregate of primary silica particles that can be broken by mechanical action. In other words, the term "particles" refers to assemblies/aggregates of indivisible primary particles, said aggregates being defined by the claimed FWHM while the indivisible primary particles are defined by their claimed average size. The aggregates preferably have a core/shell structure. Advantageously, the core is composed of larger primary particles than the shell, said core being hence more friable.

The precipitated silica that are used in the tire elastomeric compositions of the invention has primary particles having a size d_{ZS} measured by SAXS (Small Angle X-ray Scattering as described below) below 15 nm, preferably below 14 nm, more preferably below 13 nm. Generally, the size of the primary particles is above 4 nm, preferably above 5 nm and more preferably above 6 nm. Certain suitable ranges for d_{ZS} are between 5 and 15 nm, preferably between 6 and 14 nm, possibly from 6 to 13 nm, from 7 to 13 nm, from 6 to 12 nm, from 7 to 12 nm, from 6 to 11 nm, from 7 to 11 nm, from 6 to 10 nm or from 7 to 10 nm. Typically, the primary particles of the silica according to the invention all have a particle size in the same range (generally between 5 and 15 nm, preferably between 6 and 14 nm, more preferably between 5 and 11 nm and still more preferably between 6 and 10 nm), meaning in fact that there is one population of primary particles.

The L_d of the precipitated silica that are used in the tire elastomeric compositions of the invention is typically at least 1.00, preferably at least 1.25, more preferably at least 1.50. This L_d is generally below 2.10, typically below 2.00. The L_d of the inventive silica used in the tire elastomeric compositions of the invention is preferably between 1.00 and 2.00, more preferably between 1.50 and 1.90. The L_d is defined as follows: $L_d = (d_{84}-d_{16})/d_{50}$, wherein d_n is the particle diameter below which one finds n% of the total measured mass. L_d is an adimensional number calculated on the cumulative particle size curve.

Parameter FWHM, determined by means of centrifugal sedimentation in a disc centrifuge using a CPS as detailed hereafter, is used to define the width of the particle size distribution of the precipitated silica used in the tire elastomeric compositions of the invention. FWHM (or Full Width at Half Maximum) is obtained from the CPS differential curve. The FWHM measures the distribution width of silica objects around an average size defined by the mode (in nm). If FWHM is large around the average value, the silica product is heterogeneous. If the FWHM is sharp around the average value, the silica product is more homogeneous. In case of a Gaussian particle size distribution (which is barely the case in practice), parameter FWHM is correlated to parameter L_d.

The FWHM of the precipitated silica according to the invention is generally of at least 80, very often of at least 90 nm, often of at least 100 nm and sometimes of at least 110 nm. Besides, parameter FWHM is generally of at most 300 nm, very often of at most 250 nm, often of at most 200 nm, and possibly of at most 190 nm, at most 180 nm, at most 170 nm or at most 160 nm. Good results were obtained with a FWHM ranging from 100 nm to 250 nm.

As above specified, the parameter FWHM of the precipitated silica according to the invention complies with relation (I):

$$|\,\text{FWHM}\,| > -0.16 \times |\,\text{CTAB}\,| + 130 \qquad \text{(I)}$$

Possibly, the parameter FWHM of the precipitated silica according to the invention complies with relation (I_1):

$$|\,\text{FWHM}\,| > k_1 \times -0.16 \times |\,\text{CTAB}\,| + 130 \qquad (I_1)$$

wherein k_1 is an adimensional number which is equal to 1.20.

Besides, the parameter FWHM of the precipitated silica according to the invention usually complies with relation (I_2):

$$|\,\text{FWHM}\,| < k_2 \times -0.16 \times |\,\text{CTAB}\,| + 130 \qquad (I_2)$$

wherein k_2 is an adimensional number which is equal to 3.00.

Often, the parameter FWHM of the precipitated silica according to the invention complies with relation (I_3):

$$| \mathrm{FWHM} | < k_3 \times -0.16 \times | \mathrm{CTAB} | + 130 \qquad (I_3)$$

wherein k_3 is an adimensional number which is equal to 2.20.

Sometimes, the parameter FWHM of the precipitated silica according to the invention complies with relation (I_4):

$$| \mathrm{FWHM} | < k_4 \times -0.16 \times | \mathrm{CTAB} | + 130 \qquad (I_4)$$

wherein k_4 is an adimensional number which is equal to 1.80.

The FWHM of the precipitated silica according to the invention may comply with relations (I) and (I_2). It may also comply with relations (I) and (I_3). It may also comply with relations (I) and (I_4). It may also comply with relations (I_1) and (I_2). It may also comply with relations (I_1) and (I_3). It may also comply with relations and (I_1) and (I_4).

The d_{50} of the precipitated silica according to the invention is determined by means of centrifugal sedimentation in a disc centrifuge using a CPS as detailed hereafter. d_{50} actually represents the particle diameter below (and above) which 50% of the total mass of particles is found. Thus, d_{50} represents the median particle size of a given distribution, wherein the term “size” in this context has to be intended as “diameter”.

The d_{50} of the inventive silica that are used in the tire elastomeric compositions of the invention is preferably characterised by the following relation: $|d_{50}| > -0.81x\ |\mathrm{CTAB}| + 263$ (IV).

Typically, this d_{50} is comprised between 110 nm and 240 nm, preferably between 130 and 220 nm.

The d_{84} of the inventive silica used in the tire elastomeric compositions of the invention is preferably characterised by the following relation: $|d_{84}| < 2.81\ x\ |\mathrm{FWHM}| + 35$ (V).

Typically, this d_{84} is comprised between 200 and 550 nm, preferably between 250 and 500 nm.

The rate of fines (τf), that is to say the proportion (by weight) of particles of a size less than 1 μm after deagglomeration by ultrasounds (determined by the “sedigraph” test method described below), is also a way illustrate the ability to disperse of the precipitated silica that are used in the tire elastomeric compositions of the invention. According to the invention, τf is of at least 91%. In a preferred embodiment, this rate of fines τf is of at least 92%. The rate of fines τf is more preferably of at least 94% and still more preferably of at least 95%; in some especially preferred embodiments, τf may be of at least 96%, at least 97%, of at least 98% or of at least 99%. Often, τf is of at most 99%; sometimes, it is of at most 98%. Certain suitable ranges for the rate of fines τf are from 95% to 99% and from 96% to 99%. It is understood that these values can apply to any precipitated silica, irrespectively of its form. They can notably apply to a product which has not been granulated i.e. to powder or to micropearls. They can also apply to granules.

Precisely, the form of the precipitated silica used in the tire elastomeric composition of the invention is not particularly limited. Said silica can thus be notably in a form selected from the group consisting of a powder, substantially spherical beads (commonly referred to as “micropearls”), granules and mixtures thereof. In some embodiments, it is the form of a powder. In some other embodiments, it is in the form of micropearls. In still other embodiments, it is in the form of granules.

Surprisingly, the morphology of said precipitated silica and its specific distribution of its particles lead to obtain tire elastomeric compositions having a good compromise of different mechanical properties that are sometime conflicting to each other. Indeed, for example, the skilled person in the art knowns that one of the requirements needed for a tyre is to provide optimal grip on the road, especially on wet ground. One way of giving the tyre increased grip on wet ground is to use an elastomeric composition in its tread, which composition has a broad hysteresis potential. But at the same time, the tyre tread must also minimize its contribution to the rolling resistance of the tyre, that is to say have the lowest possible hysteresis. Surprisingly, the specific precipitated silica used in the tire elastomeric compositions of the present invention may have notably both good grip on wet ground and good rolling resistance. The tire elastomeric compositions of the invention may have advantageously good wear properties (evaluated by the measurement of tensile strength and deformation at break) while maintaining a good grip on wet ground.

The precipitated silica used in the tire elastomeric compositions of the invention is advantageously obtained by a process comprising:

(i) providing a starting solution having a pH from 2.00 to 5.50,

(ii) simultaneously adding a silicate and an acid to said starting solution to obtain a reaction medium of which the pH is maintained in the range from 2.00 to 5.50,

(iii) stopping the addition of the acid and of the silicate and adding a base to the reaction medium to raise the pH of said reaction medium to a value from 7.00 to 10.00,

(iv) simultaneously adding to the reaction medium a silicate and an acid, such that the pH of the reaction medium is maintained in the range from 7.00 to 10.00,

(v) stopping the addition of the silicate while continuing the addition of the acid to the reaction medium to reach a pH of the reaction medium of less than 6.00 and obtaining a suspension of precipitated silica,

wherein step (i) comprises the following steps:

(ia) providing an aqueous medium eventually comprising an electrolyte as initial stock,

(ib) simultaneously adding to this aqueous medium a silicate and an acid, such that the pH of the aqueous medium is maintained in the range from 7.00 to 10.00, wherein the amount of silicate added to the aqueous medium is between 1% and 10% of the total amount of silicate required for the reaction, preferably between 5% and 9% of the total amount of silicate required for the reaction,

(ic) stopping the addition of silicate while continuing the addition of the acid to the aqueous medium obtained in step (ib) in order to provide the starting solution having a pH from 2.00 to 5.50.

The total amount of silicate to obtain a given final amount of silica can be determined by the person skilled in the art at the beginning of the process according to common general knowledge. The amount of silicate added during step (ib) will be designated below as AS0 silicate ratio.

The term “base” is used herein to refer to one or more than one base which can be added during the course of said process and it includes the group consisting of silicates as defined hereafter. Any base may be used in the process. In addition to silicates, notable non-limiting examples of suitable bases are for instance alkali metal hydroxides and ammonia. Preferably, the base is a silicate and more preferably, the same silicate as the one used in the process.

The term “silicate” is used herein to refer to one or more than one silicate which can be added during the course of said process. The silicate is typically selected from the group consisting of the alkali metal silicates. The silicate is advantageously selected from the group consisting of sodium and potassium silicate. The silicate may be in any known form, such as metasilicate or disilicate. It can be sourced from diverse materials like sand, natural sources containing silica, either combusted (like RHA or Rice Hull Ash) or as such, and even from waste (from construction, mining etc.).

In the case where sodium silicate is used, the latter generally has a SiO_2/Na_2O weight ratio of from 2.0 to 4.0, in particular from 2.4 to 3.9, for example from 3.1 to 3.8.

The silicate may have a concentration (expressed in terms of SiO_2) of from 3.9 wt% to 25.0 wt%, for example from 5.6 wt% to 23.0 wt%, in particular from 5.6 wt% to 21.0 wt%.

The term "acid" is used herein to refer to one or more than one acid which can be added during the course of said process. Any acid may be used in the process. Use is generally made of a mineral acid, such as sulfuric acid, nitric acid, phosphoric acid or hydrochloric acid, or of an organic acid, such as a carboxylic acid, e.g. acetic acid, formic acid or carbonic acid. Good results were obtained with sulphuric acid.

The acid may be metered into the reaction medium in diluted or concentrated form. The same acid at different concentrations may be used in different stages of the process. Preferably, a diluted acid is used until the gel point is reached (which happens during step (ii)) and a concentrated acid is used after the point of gel is reached. Preferably, the dilute acid is dilute sulfuric acid (i.e. with a concentration very much less than 80% by mass, preferably a concentration of less than 20% by mass, in general less than 14% by mass, in particular of not more than 10% by mass, for example between 5% and 10% by mass). Advantageously, the concentrated acid is concentrated sulfuric acid, i.e. sulfuric acid with a concentration of at least 80% by mass (and in general of not more than 98% by mass), preferably of at least 90% by mass; in particular, its concentration is between 90% and 98% by mass, for example between 91% and 97% by mass.

In a preferred embodiment of the process sulfuric acid and sodium silicate are used in all of the stages of the process. Preferably, the same sodium silicate, that is sodium silicate having the same concentration expressed as SiO_2, is used in all of the stages of the process.

In step (i) of the process a starting solution having a pH from 2.00 to 5.00 is provided in the reaction vessel. Preferably, the starting solution has a pH from 2.50 to 5.00, especially from 3.00 to 4.50; for example, the starting solution has a pH from 3.50 to 4.50.

According to said process, this starting solution is prepared using namely the following steps (ia) to (ic) as described above.

Without willing to be bound by a theory, the Applicant believes that during these sub-steps of step (i), bigger primary particles are generated than in the subsequent steps of the process (namely during steps (ii) and (iv)) which allows reaching inhomogeneous aggregates with a large particle size distribution.

The starting solution of step (i) may or may not comprise an electrolyte. Preferably, the starting solution of step (i) contains an electrolyte in order to help recycling water streams in the process.

The term "electrolyte" is used herein in its generally accepted meaning, i.e. to identify any ionic or molecular substance which, when in solution, decomposes or dissociates to form ions or charged particles. The term “electrolyte” is used herein to indicate that one or more than one electrolyte may be present. Mention may be made of electrolytes such as the salts of alkali metals and alkaline-earth metals. Advantageously, the electrolyte for use in the starting solution is the salt of the metal of the starting silicate and of the acid used in the process. Notable examples are for example sodium chloride, in the case of the reaction of a sodium silicate with hydrochloric acid or, preferably, sodium sulfate, in the case of the reaction of a sodium silicate with sulfuric acid. Preferably, the electrolyte does not contain aluminium.

Preferably, when sodium sulfate is used as electrolyte in step (i), its concentration in the starting solution is from 5 to 40 g/L, especially from 8 to 30 g/L, for example from 10 to 25 g/L.

Step (ii) of the process comprises a simultaneous addition of an acid and of a silicate to the starting solution. The rates of addition of the acid and of the silicate during step (ii) are controlled in such a way that the pH of the reaction medium is maintained in the range from 2.00 to 5.50. The pH of the reaction medium is preferably maintained in the range from 2.50 to 5.00, especially from 3.00 to 5.00, for example from 3.20 to 4.80.

The simultaneous addition in step (ii) is advantageously performed in such a manner that the pH value of the reaction medium is always equal (to within ± 0.20 pH units) to the pH reached at the end of step (i).

Preferably, step (ii) consists of a simultaneous addition of acid and silicate as detailed above. Generally, a point of gel is reached during step (ii). In one embodiment, the amount of silicate added during step (ii) after the point of gel is reached is between 5% and 55% of the total amount of silicate added during step (ii), preferably between 10% and 50% and more preferably 15% and 45% of the total amount of silicate added during step (ii). The point of gel is defined as the point where the reaction medium undergoes an abrupt change in viscosity, which can be determined by measuring the torque on the agitator. Generally, the agitation torque increases by a value between 20% and 60% compared to the torque value before the point of gel, preferably by a value between 25% and 55%, more preferably by a value between 30% and 50% compared to the torque value before the point of gel.

Next, in step (iii), the addition of the acid and of the silicate is stopped and a base is added to the reaction medium. The addition of the base is stopped when the pH of the reaction medium has reached a value of from 7.00 to 10.00, preferably from 7.50 to 9.50.

In a first embodiment of the process the base is a silicate. Thus, in step (iii), the addition of the acid is stopped while the addition of the silicate to the reaction medium is continued until a pH of from 7.00 to 10.00, preferably from 7.50 to 9.50, is reached.

In a second embodiment of the process the base is different from a silicate and it is selected from the group consisting of the alkali metal hydroxides, preferably sodium or potassium hydroxide. When sodium silicate is used in the process a preferred base may be sodium hydroxide.

Thus, in this second embodiment of the process, in step (iii), the addition of the acid and of the silicate is stopped and a base, different from a silicate, is added to the reaction medium until a pH of from 7.00 to 10.00, preferably from 7.50 to 9.50, is reached.

At the end of step (iii), that is to say after stopping the addition of the base, it may be advantageous to perform a maturing step of the reaction medium. This step is preferably carried out at the pH obtained at the end of step (iii). The maturing step may be carried out while stirring the reaction medium. The maturing step is preferably carried out under stirring of the reaction medium over a period of 2 to 45 minutes, in particular from 5 to 25 minutes. Preferably the maturing step does not comprise any addition of acid or silicate.

After step (iii) and the optional maturing step, a simultaneous addition of an acid and of a silicate is performed, such that the pH of the reaction medium is maintained in the range from 7.00 to 10.00, preferably from 7.50 to 9.50.

The simultaneous addition of an acid and of a silicate (step (iv)) is typically performed in such a manner that the pH value of the reaction medium is maintained equal to the pH reached at the end of the preceding step (to within ± 0.20 pH units), namely step (iii).

Preferably, the amount of silicate added to the reaction medium during step (iv) is at least 45% of the total amount of silicate required for the reaction.

It should be noted that said process may comprise additional steps. For example, between step (iii) and step (iv), and in particular between the optional maturing step following step

(iii) and step (iv), an acid can be added to the reaction medium. The pH of the reaction medium after this addition of acid should remain in the range from 7.00 to 9.50, preferably from 7.50 to 9.50.

In step (v), the addition of the silicate is stopped while continuing the addition of the acid to the reaction medium so as to obtain a pH value in the reaction medium of less than 6.00, preferably from 3.00 to 5.50, in particular from 3.00 to 5.00. A suspension of precipitated silica is obtained in the reaction vessel.

At the end of step (v), and thus after stopping the addition of the acid to the reaction medium, a maturing step may advantageously be carried out. This maturing step may be carried out at the same pH obtained at the end of step (v) and under the same time conditions as those described above for the maturing step which may be optionally carried out between step (iii) and (iv) of the process.

The reaction vessel in which the entire reaction of the silicate with the acid is performed is usually equipped with adequate stirring and heating equipment.

The entire reaction of the silicate with the acid (steps (i) to (v)) is generally performed at a temperature from 40 to 97°C, in particular from 60 to 95°C, preferably from 80 to 95°C, more preferably from 85 to 95°C.

According to one variant of said process, the entire reaction of the silicate with the acid is performed at a constant temperature, usually from 40 to 97°C, in particular from 80 to 95°C, and even from 85 to 95°C.

According to another variant of said process, the temperature at the end of the reaction is higher than the temperature at the start of the reaction: thus, the temperature at the start of the reaction (for example during steps (i) to (iii)) is preferably maintained in the range from 40 to 85°C and the temperature is then increased, preferably up to a value in the range from 80 to 95°C, even from 85 to 95°C, at which value it is maintained (for example during steps (iv) and (v)), up to the end of the reaction.

At the end of the steps that have just been described, a suspension of precipitated silica is obtained, which is subsequently separated (liquid/solid separation). The process typically comprises a further step (vi) of filtering the suspension and drying the precipitated silica.

The separation performed in said preparation process usually comprises a filtration, followed by washing, if necessary. The filtration is performed according to any suitable method, for example by means of a belt filter, a rotary filter, for example a vacuum filter, or, preferably a filter press.

The filter cake is then subjected to a liquefaction operation. The term “liquefaction” is intended herein to indicate a process wherein a solid, namely the filter cake, is converted into a fluid-like mass generally by adding a liquid to it. After the liquefaction step the filter cake is in a flowable, fluid-like form and the precipitated silica is in suspension.

The liquefaction step may comprise a mechanical treatment which results in a reduction of the granulometry of the silica in suspension. Said mechanical treatment may be carried out by passing the filter cake through a high shear mixer, a colloidal-type mill or a ball mill. Alternatively, the liquefaction step may be carried out by subjecting the filter cake to a chemical action by addition for instance of an acid or an aluminium compound, for example sodium aluminate. Still alternatively, the liquefaction step may comprise both a mechanical treatment and a chemical action.

The suspension of precipitated silica which is obtained after the optional liquefaction step is subsequently preferably dried, eventually after having been treated by additional chemical(s), like organic one(s) for instance (e.g. polycarboxylic acids).

This drying may be performed according to means known in the art. Preferably, the drying is performed by atomization. To this end, use may be made of any type of suitable atomizer, in particular a turbine, nozzle, liquid pressure or two-fluid spray-dryer. In general, when the filtration is performed using a filter press, a nozzle spray-dryer is used, and when the filtration is performed using a vacuum filter, a turbine spray-dryer is used.

When the drying operation is performed using a nozzle spray-dryer, the precipitated silica that may then be obtained is usually in the form of substantially spherical beads, commonly referred to as “micropearls”. After this drying operation, it is optionally possible to perform a step of milling or micronizing on the recovered product; the precipitated silica that may then be obtained is generally in the form of a powder. After this drying operation, it is also optionally possible to perform a step wherein the recovered micropearls are subjected to an agglomeration step, which consists, for example, of direct compression, wet granulation, extrusion or, preferably, dry compacting; the precipitated silica that is then obtained is generally in the form of granules.

When the drying operation is performed using a turbine spray-dryer, the precipitated silica that may then be obtained may be in the form of a powder.

In one embodiment of said process, the filter cake is not submitted to a liquefaction step but is directly dried by spin flash drying (for instance by Hosokawa type process).

Finally, the dried, milled or micronized product as indicated previously may optionally be subjected to an agglomeration step, which consists, for example, of direct compression, wet granulation (i.e. with use of a binder, such as water, silica suspension, etc.), extrusion or, preferably, dry compacting.

The precipitated silica that may then be obtained via this agglomeration step is generally in the form of granules.

The proportion by weight of the inventive precipated silica used in the tire elastomeric compositions of the invention can vary within a fairly wide range. It normally represents from 1 phr to 250 phr, in particular from 5 phr to 200 phr, especially from 10 phr to 170 phr, for example from 20 phr to 140 phr or even from 25 phr to 130 phr, or alternatively from 10 phr to 40 phr

The inventive precipitated silica used in the tire elastomeric compositions of the invention then preferably constitutes at least 30% by weight, preferably at least 60%, indeed even at least 80% by weight, of the total amount of the weight of the reinforcing filler of the tire elastomeric composition.

The inventive precipitated silica used in the tire elastomeric compositions of the invention can advantageously constitute all of the reinforcing inorganic filler of the tire elastomeric composition.

The inventive precipitated silica used in the tire elastomeric compositions of the invention can optionally be combined with at least one other reinforcing filler, for instance with a conventional or a highly dispersible silica, such as Zeosil® Premium SW, Zeosil® Premium 200MP, Zeosil® 1165MP, Zeosil® 1115MP or Zeosil® 1085 GR (commercially available from Solvay), or another reinforcing inorganic filler, such as nanoclays, alumina. Alternatively, the silica used in the tire elastomeric compositions of the invention may be combined with an organic reinforcing filler, such as carbon black nanotubes, graphene, starch, cellulose, carbon black and the like.

All carbon blacks can be used in the tire elastomeric compositions of the invention, especially blacks of the HAF, ISAF or SAF type, conventionally used in tyres ("tyre-grade" blacks) are suitable as carbon blacks. Mention will more particularly be made, among the latter, of the reinforcing carbon blacks of the 100, 200 or 300 series (ASTM grades), such as, for example, the N115, N134, N234, N326, N330, N339, N347 or N375 blacks, or else, depending on the applications targeted, the blacks of higher series (for example N660, N683 or N772). The carbon blacks might, for example, be already incorporated in an elastomer, especially an isoprene elastomer, in the form of a masterbatch (see, for example, applications WO 97/36724 or WO 99/16600).

When it is present, the carbon black is preferentially used in a content within a range extending from 0.1 to 10 phr, more preferentially from 0.5 to 10 phr, notably from 1 to 8 phr.

The amount of the total reinforcing filler (that is to say the amount of inventive silica used in the tire elastomeric compositions and the amount of carbon black when it is present or other reinforcing filler when they are present) are in the range extending from 1 to 260 phr, in particular from 5 phr to 210 phr especially from 10 phr to 180 phr, for example from 20 phr to 150 phr or even from 25 phr to 140 phr, even more preferably 50 to 140 phr.

The inventive silica used in the tire elastomeric compositions of the invention is defined by a marked ability to disperse in elastomeric compositions. A known method to determine the ability of a filler to disperse in an elastomeric matrix is described in S. Otto et al. in Kautschuk Gummi Kunststoffe, 58 Jahrgang, NR 7-8 / 2005. The method, described in more details hereafter, relies on optical analysis and defines the dispersion of the filler in the elastomeric matrix in terms of a Z value which is proportional to the amount of undispersed filler in a matrix, with 100 indicating a perfect mix and 0 a poor mix.

The tire elastomeric composition of the invention comprising at least one inventive precipitated silica as defined above have advantageously higher , Z value than that of comparable mixtures containing prior art silica.

The tire elastomeric compositions of the present invention comprise at least one coupling agent between the (dienic) elastomer and the precipitated silica. In some embodiment, the tire elastomeric compositions of the present invention may preferably further comprise at least one covering agent.

Non-limiting examples of suitable coupling agents between the (dienic) elastomer and the precipitated silica are for instance "symmetrical" or "unsymmetrical" silane polysulfides; mention may more particularly be made of bis((C1-C4)alkoxyl(C1-C4)alkylsilyl(C1-C4)alkyl) polysulfides (in particular disulfides, trisulfides or tetrasulfides), such as, for example, bis(3-(trimethoxysilyl)propyl) polysulfides or bis(3-(triethoxysilyl)propyl) polysulfides, such bis(3-triethoxysilylpropyl) tetrasulfide, abbreviated to TESPT, of formula $[(C_2H_5O)_3Si(CH_2)_3S_2]_2$, or bis(triethoxysilylpropyl) disulfide, abbreviated to TESPD, of formula $[(C_2H_5O)_3Si(CH_2)_3S]_2$.. Mention may also be made of monoethoxydimethylsilylpropyl tetrasulfide, and Mention may also be made of silanes comprising masked or free thiol functional groups (likeNXT™ or NXT(TM) Z45 silanes), of mercaptopropyltriethoxysilane, and of a mixture mercaptopropyltriethoxysilane+octyltriethoxysilane (like SI 363® from Evonik).

The coupling agent can be grafted beforehand to the (dienic) elastomer. It can also be employed in the free state (that is to say, not grafted beforehand) or grafted at the surface of the silica. It is the same for the optional covering agent. In case a coupling agent is added to the silica after drying (i.e. grafted on it), it generally is an ethoxy- or a chloro- silane.

The coupling agent can optionally be combined with an appropriate "coupling activator", that is to say a compound which, mixed with this coupling agent, increases the effectiveness of the latter.

The tire elastomeric compositions of the invention may optionally also comprise all or a portion of the usual additives customarily used in elastomeric compositions intended for the manufacture of tyres or semi-finished articles for tyres, such as, for example, pigments, protection agents, such as anti-ozone waxes, chemical anti-ozonants or antioxidants, anti-fatigue agents, crosslinking agents other than those mentioned above, reinforcing resins or plasticizing agents, methylene acceptors (for example, phenolic novolak resin) or methylene donors (for example, HMT or H3M), such as described, for example, in application WO 02/10269.

For example, said additional additives may be oligomers of SBR, BR, IR, …, activators (Stearic acid, zin oxide), processing aids (fatty acids, zinc soaps, PEG, …), wax (PE wax) acting as protector, antioxydants, UV protectors and antiozonants such as 6PPD, TMQ...

Preferably, when the tire elastomeric compositions of the invention comprise a plasticizing agent, it is selected from the group consisting of solid hydrocarbon-based resins (or plasticizing resins such as terpenes, C5 resins, … commercial denomination Wingtack, Dercolyte, …), extending oils (plasticizing oils) or a mixture of plasticizing oils and resins.

In one embodiment, the tire elastomeric compositions according to the invention may further comprise at least one plasticizing agent, the amount of said plasticizing agent being in the range extending from 10 to 150 phr, preferably from 20 to 100 phr, more preferably from 30 to 85 phr.

The tire elastomeric compositions of the invention comprise at least one chemical crosslinking system. Any type of crosslinking system known to those skilled in the art for elastomeric compositions may be used.

The tire elastomeric compositions can be vulcanized with sulfur or crosslinked, in particular with peroxides or other crosslinking systems (for example diamines or phenolic resins).

The crosslinking system is preferably a vulcanization system, that is to say a system based on sulfur (or on a sulfur-donating agent) and on a primary vulcanization accelerator. Various known secondary vulcanization accelerators or vulcanization activators, such as zinc oxide, stearic acid or equivalent compounds, or guanidine derivatives (in particular diphenylguanidine), may be added to this base vulcanization system, being incorporated during the first non-productive phase and/or during the productive phase, as described subsequently.

When sulfur is used, it is used at a preferential content of between 0.5 and 12 phr, in particular between 1 and 10 phr. The primary vulcanization accelerator is used at a preferential content of between 0.5 and 10 phr, more preferentially of between 0.5 and 5.0 phr.

The vulcanization system of the tire elastomeric compositions of the invention may also comprise one or more additional accelerators, for example compounds of the family of the thiurams, zinc dithiocarbamate derivatives, sulfenamides, guanidines or thiophosphates. Use may in particular be made of any compound capable of acting as accelerator of the vulcanization of diene elastomers in the presence of sulfur, especially accelerators of thiazoles type and also their derivatives, accelerators of the thiurams type, and zinc dithiocarbamates. These accelerators are, for example, selected from the group consisting of 2-mercaptobenzothiazole disulfide (abbreviated to MBTS), tetrabenzylthiuram disulfide (TBZTD), N-cyclohexyl-2-benzothiazolesulfenamide (CBS), N,N-dicyclohexyl-2-benzothiazolesulfenamide (DCBS), N-(tert-butyl)-2-benzothiazolesulfenamide (TBBS), N-(tert-butyl)-2-benzothiazolesulfenimide (TBS), zinc dibenzyldithiocarbamate (ZBEC) and the mixtures of these compounds. Preferably, use is made of a primary accelerator of the sulfenamide type.

The tire elastomeric compositions of the invention comprising the precipitated silica may be used for the manufacture of a number of articles. Non-limiting examples of semi-finished or finished articles comprising at least one of the tire elastomeric compositions described above, are or part(s) of tires, e.g. tire treads, the latter being preferred.

The tire elastomeric compositions of the invention, intended especially for the manufacture of tyres or of semi-finished products for tyres, may be produced by any process well known to those skilled in the art.

For example, these tire elastomeric compositions of the invention may be produced in appropriate mixers, using two successive phases of preparation according to a general procedure well known to those skilled in the art: a first phase of thermomechanical working or kneading (sometimes referred to as a "non-productive" phase) at high temperature, up to a maximum temperature (denoted Tmax) of between 130°C and 200°C, preferably between 145°C and 185°C, followed by a second phase of mechanical working (sometimes referred to as a "productive" phase) at lower temperature, typically below 120°C, for example between 60°C and 100°C, during which finishing phase the crosslinking or vulcanization system is incorporated; such phases have been described, for example, in applications EP-A-0501227, EP-A-0735088 and EP-A-0810258.

For example, in a process for preparing the tire elastomeric compositions of the invention, said precipitated silica as being described above, combined or not combined with another reinforcing inorganic filler, such as an additional silica for example, or with carbon black and the agent for coupling the (dienic) elastomer to silica, are incorporated by kneading to the elastomer (preferably (dienic) elastomer or (dienic) elastomers) during the first "non-productive" phase, that is to say that at least these ingredients are introduced into the mixer and thermomechanically kneaded, in one or several goes. Then, after for example one to two minutes of kneading, the optional additional covering agents or processing aids and other various additives, with the exception of the crosslinking or vulcanization system, are added to the internal mixer. This mixture is thermomechanically kneaded until the abovementioned maximum temperature Tmax is reached. It is possible to envisage one or more additional steps with the aim of preparing masterbatches of elastomers/reinforcing fillers intended to be introduced during the first "non-productive" phase. The masterbatches of elastomers/reinforcing fillers comprising at least one inventive precipitated silica may preferably be obtained by bulk mixing or liquid mixing starting from an elastomer latex and an aqueous dispersion of said reinforcing filler.

The mixture is then cooled, and the crosslinking system (preferably the vulcanization system) is then incorporated at low temperature (typically less than 100°C), generally in an external mixer, such as an open mill; the combined mixture is then mixed for a few minutes, for example between 5 and 15 min. This second phase is the “productive” phase.

The process for preparing a tire elastomer compositions of the invention preferably comprises the following stages:

- at least one elastomer, preferably (dienic) elastomer, at least one reinforcing filler and at least one agent for coupling the elastomer to the precipitated silica are brought into contact; said reinforcing filler comprising a precipitated silica having:
    - a CTAB surface area in the range from 40 to 525 m^2/g;
    - primary particles having an average size measured by SAXS below 15 nm;
    - an amount of aluminium W_{Al} of at least 0.50wt%,
    - a proportion (by weight) of particles of a size less than 1µm after deagglomeration by ultrasounds, which is of at least 91%; and
    - a particle size distribution measured by centrifugal sedimentation using a CPS, such that for a given value of the CTAB surface area, parameter FWHM is defined by relation (I):
      $| \text{FWHM} | > -0.16 \times | \text{CTAB} | + 130$ (I),
- these ingredients being kneaded thermomechanically, once or several times, until a maximum temperature of between 110°C and 190°C is reached;
- the mixture from the preceding step is cooled to a temperature below 100°C,
- a crosslinking system is incorporated into the cooled mixture from the preceding step,
- the mixture comprising the crosslinking system is kneaded up to a maximum temperature below 110°C.

The final composition thus obtained is subsequently calendered, for example in the form of a sheet or slab, especially for laboratory characterization, or else extruded, in order to form, for example, a rubber profiled element used in the manufacture of semi-finished products especially for tyres. These products may then be used for the manufacture of tyres, according to techniques known to those skilled in the art, with the advantage of the invention, namely a good mechanical properties compromise.

Preferably, the process for preparing a tire elastomeric compositions of the invention also comprises a step in which the kneaded mixture comprising the crosslinking system is cured.

This curing (or vulcanization) step is carried out according to methods well known to those skilled in the art. It is especially carried out in a known way at a temperature generally of between 130°C and 200°C, under a pressure of several hundred bar, for a sufficient time which may be within a range extending, for example, between 5 and 90 min, depending especially on the curing temperature, on the crosslinking system adopted, on the kinetics of vulcanization of the composition in question or else on the size of the tyre.

Another subject of the present invention relates to a semi-finished article, especially for a tyre, comprising at least one tire elastomeric compositions of the invention as defined above. The semi-finished articles of the present invention advantageously have namely a good mechanical properties compromise.

The tire elastomeric compositions of the semi-finished product may either be in the uncured state (before crosslinking) or in the cured state (after crosslinking).

The semi-finished article may be any article of use for the manufacture of finished rubber articles for tyre.

Preferentially, the semi-finished article for a tyre may be selected from underlayers, bonding rubbers between rubbers of different natures or calendering rubbers for metal or textile reinforcers, sidewall rubbers or treads. More preferentially, the semi-finished article is a tyre tread. The tyre tread may comprise at least one tire elastomeric composition defined above. The tire elastomeric compositions of the invention can constitute the whole semi-finished product or else part of the semi-finished article. Preferably the tire elastomeric compositions of the invention can constitute the whole tread or else part of the tread.

The semi-finished articles are obtained by methods well known to those skilled in the art.

Another subject of the present invention relates to a tyre comprising at least one tire elastomeric composition in accordance with the invention as described above or comprising at least one semi-finished article as described above. The tyres of the present invention advantageously have namely a good mechanical properties compromise.

The tyres of the invention may especially be intended to equip motor vehicles of the passenger vehicle, SUV (“*Sports Utility Vehicles*”), SUT (“*Sports Utility Truck*”), two-wheel vehicle (especially motorcycle) or aircraft type, and industrial vehicles chosen from vans, heavy-duty vehicles, that is to say, underground trains, buses, heavy road transport vehicles (lorries, tractors, trailers) or off-road vehicles, such as heavy agricultural or construction plant vehicles, and other transportation or handling vehicles.

The tyres of the invention are obtained by methods well known to those skilled in the art.

Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

ANALYTICAL METHODS

The physicochemical properties of the precipitated silica used in the tire elastomeric compositions of the invention were determined using the methods described hereafter.

Possible pretreatment of the precipitated silica

When the precipitated silica is in a form of highly agglomerated particles, typically when the precipitated silica is in a form other than a powder, a pretreatment thereof is desirable before applying certain analytical methods, such as a method for determining CTAB surface area and/or a method for determining the primary particles size by SAXS (both methods of concern being detailed here below).

In particular, on the one hand, when the precipitated silica is in the form of micropearls, that is to say a first form of highly agglomerated particles, it is desirable, before applying the method for determining the primary particles size by SAXS, to deagglomerate the micropearls so as to obtain a precipitated silica sample in the form of a powder.

On the other hand, when the precipitated silica is in the form of granules, that is to say another form of highly agglomerated particles, it is desirable, before applying the method for determining the primary particles size by SAXS and also before applying the method for determining CTAB surface area, to deagglomerate the granules so as to obtain a precipitated silica sample in the form of a powder.

In both cases, the same deagglomeration pretreatment was applied, which one is detailed hereinafter.

Deagglomeration pretreatment for a precipitated silica in a form of highly agglomerated particles, especially in the form of micropearls or granules. Precipitated silicas samples in a form of highly agglomerated particles, especially in the form of granules or micropearls, were smoothly ground using a hand agate mortar and a hand agate pestle, applying manually smooth pressure and friction on the silica samples so as to cause the destruction of the agglomerates and other lumps contained therein. The grinding was operated for a duration sufficient for the samples to acquire a visually homogeneous consistency which was that of a powder; this duration was generally of a few tens of seconds and did not generally exceed 1 min.

For the sake of clarity, the above pretreatment should not be operated when the precipitated silica is in the form of a powder. The above pretreatment could but needs not, and thus shall generally not be operated when applying a method for the determination of BET surface area, a method for the determination of the rate of fines by “sedigraph”, a method for the determination of the amount of aluminium W_{Al} or a method for the determination of water moisture (all such methods being as below detailed) to the precipitated silica, irrespectively of its form. The above pretreatment could also be but needs not, and thus shall generally not be operated when applying a method for determining CTAB surface area to a precipitated silica in the form of micropearls.

Determination of CTAB surface area

CTAB surface area (S_{CTAB}) values were determined according to an internal method derived from standard NF ISO 5794-1, Appendix G. The method was based on the adsorption of CTAB (N hexadecyl-N,N,N-trimethylammonium bromide) on the "external" surface of the silica.

In the method, CTAB was allowed to adsorb on silica under magnetic stirring. Silica and residual CTAB solution were then separated. Excess, unadsorbed CTAB, was determined by back-titration with bis(2-ethylhexyl)sulfosuccinate sodium salt (hereinafter "AOT") using a titroprocessor, the endpoint being given by the turbidity maximum of the solution and determined using an optrode.

Equipment

Metrohm Optrode (Wavelength : 520 nm) connected to photometer 662 Metrohm; Metrohm Titrator: Titrino DMS 716; Metrohm titration software: Tiamo.

Glass beaker (2000 mL); volumetric flasks (2000 mL); sealed glass bottles (1000 and 2000 mL); disposable beakers (100 mL); micropipette (500 – 5000 µL); magnetic stirring bars with 25 mm discs ends (Ref VWR 442-9431) for adsorption; magnetic stirring bars (straight) for titration; polycarbonate centrifugation tubes (at least 20 mL), centrifuge (allowing a 10000 rpm speed); glass vials (30 mL); thermobalance.

Preparation of the solutions

Preparation of CTAB solution: at 5.5 g/L (buffered at about pH 9.6): in a 2000 mL beaker containing about 1000 mL of distilled water at 25 °C were added: 54.25 g of boric acid solution ([c]= 4%); 2.60 g of KCl, 25.8 mL (±0.1 mL) of sodium hydroxide. The so-obtained solution was stirred for 15 min before adding 11.00 g ± 0.01 g of CTAB powder (99.9% purity, purchased from Merck). After stirring, the solution was transferred to a 2000 mL volumetric flask kept at 25°C and the volume brought at 2000 mL with distilled water. The solution was transferred in a 2000 mL glass bottle. The solution was kept at a temperature not lower than 22°C to avoid CTAB crystallization (occurring at 20 °C).

Preparation of AOT solution: about 1200 mL of distilled water in a 2000 mL beaker were heated to 35 °C under magnetic stirring. 3.7038 g of AOT (98% purity, purchased from Aldrich) were added. The solution was transferred to a 2000 mL volumetric flask and allowed to cool back to 25 °C. The volume was brought to 2000 mL with distilled water and the solution was transferred in two glass bottles of 1000 mL which were stored at 25 °C in a dark place.

All equipment and solutions were kept at 25 °C during analysis.

Procedure at the beginning and at the end of each experiment

Experiment beginning solutions were agitated before use. The dosing device was purged before use. At least 40 mL of AOT were passed through the device to ensure that the device is clean and that all the air bubbles were removed. Experiment end: purge the dosing device in order to remove the AOT solution. Clean the optrode. Soak the optrode in distilled water.

Blank factor determination

The variation of AOT and CTAB solutions concentrations, over time, are corrected through the determination of a daily 'blank factor' called ratio R1 = V1/m1.

In a 100 mL disposable beaker: 4.9000 g ± 0.0100 g of the 5.5 g/L CTAB solution (m1) were accurately weighed. The tare was set and 23.0000 g ± 1.0000 g of distilled water (M_{WATER}) were accurately added. The solution was placed under stirring using a magnetic stirrer at 500 rpm on the dosing device and the titration was started. Stirring speed must strictly be steady throughout the titration without generating too much air bubbles.

V1 is the end point volume of AOT solution required to titrate the CTAB solution m1.

The R1 determination is performed at least in duplicate. If the standard deviation of R1 = V1/m1 exceeds 0.010, the titration is repeated until the standard deviation is lower or equal to 0.010. The daily ratio R1 is calculated as the average of the 2 or 3 measurements. Note: the optrode must be washed with distilled water after every measurement and dried with absorbent paper.

CTAB adsorption on silica

The moisture content (%H_2O) for each silica sample was determined with a thermobalance (temperature :160°C) before the adsorption step as follows: tare the balance with an aluminium cup; weigh about 2 g of silica and distribute equally the powder on the cup, close the balance; note the percentage of moisture. In a 100 mL disposable beaker: 0.0100 g of silica (m0) were accurately weighed. 50.0000 mL + 1.0000 mL of the CTAB stock solution (V0) were added. The total mass was recorded. The suspension was stirred for 40 minutes ±1 minute on the stirring plate at 450 rpm using magnetic stirring bars with disc ends. After 40 minutes the sample was removed from the stirring plate.

25 to 50 mL of the suspension were transferred in a centrifuge tube (volume depends on centrifuge tube size) and they were centrifuged for 35 minutes at a 10000 rpm speed at 25 °C. After centrifugation, the tube was gently removed from the centrifuge not to unsettle the silica. 10 to 20 mL of CTAB solution were transferred in a glass vial which was then stoppered and kept at 25°C.

Titration of the CTAB solution

In a 100 mL disposable beaker = 4.0000 g ± 0.0100 g of the CTAB solution at unknown concentration (m2) were accurately weighed.

Tare was set and 19.4000 g ± 1.0000 g of distilled water (M_{water}) were added. The solution was placed under stirring at 500 rpm on the dosing device and the titration with the AOT solution was started.

V2 is the end point volume of AOT required to titrate an amount m2 of CTAB solution.

The CTAB surface area S_{CTAB} is calculated as follows:

$$S_{CTAB} = \frac{R_1 - R_2}{R_1} \times [CTAB]i \times 578.435 \times \frac{V_0}{M_{ES}}$$

wherein:

S_{CTAB} = surface area of silica (including the moisture content correction) [m^2/g]

R1 = V1/m1;

m1 = mass of the CTAB stock solution titrated as the blank (kg);

V1 = end point volume of AOT required to titrate m1 of the CTAB stock solution as the blank (L)

R2 = V2/m2;

m2 = mass of the CTAB solution titrated after adsorption and centrifugation (kg);

V2 = end point volume of AOT required to titrate m2 of the CTAB stock solution after adsorption and centrifugation (L)

[CTAB]i = Concentration of the CTAB stock solution (g/L)

V0 = Volume of the CTAB stock solution used for the adsorption on silica (L)

M_{ES} = Solid content of silica used for the adsorption (g) corrected for the moisture content as follows:

$M_{ES} = m0 \times (100 - \%H_2O) / 100$ wherein m0 = initial mass of silica (g).

Determination of BET surface area

BET surface area S_{BET} was determined according to the Brunauer - Emmett - Teller method as detailed in standard NF ISO 5794-1, Appendix E (June 2010) with the following adjustments: the sample was pre-dried at 160°C±10°C; the partial pressure used for the measurement P/P^0 was between 0.05 and 0.2.

Determination of the particle size distribution and particle size by centrifugal sedimentation in a disc centrifuge using a centrifugal photosedimentometer (CPS)

Values of d_{50}, d_{16}, d_{84}, FWHM and L_d were determined centrifugal sedimentation in a disc centrifuge using a centrifugal photosedimentometer type “CPS DC 24000UHR”, marketed by CPS Instruments company. This instrument is equipped with operating software supplied with the device (operating software version 11g).

Instruments used: for the measurement requirement, the following materials and products were used: Ultrasound system: 1500-watt generator of Sonics Vibracell VCF1500 type, equipped with a Sonics Vibracell CV154 type converter, with a Sonics Vibracell BHN15GD (x1.5) type booster, and a Sonics Vibracell 207-10 19 mm probe, with interchangeable 19 mm Sonics Vibracell 630-0407 type tip.

Analytical balance with a precision of 0.1 mg (e.g., Mettler AE260); Syringes: 1.0 ml and 2.0 ml with 20ga needles; high shape glass beaker of 50 mL (SCHOTT DURAN: 38 mm diameter, 70 mm high); magnetic stirrer with a stir bar of 2 cm; vessel for ice bath during sonication.

Chemicals: deionized water; ethanol 96%; sucrose 99%; dodecane, all from Merck; PVC reference standard from CPS Instrument Inc.; the peak maximum of the reference standard used should be between 200 and 600 nm (e.g. 239 nm).

Preparation of the disc centrifuge

For the measurements, the following parameters were established. For the calibration standard parameters, the information of the PVC reference communicated by the supplier were used:

Sample Parameters		
max.diameter	μm	0.79
min.diameter	μm	0.02
particle density	g/mL	2.11
particle refrative index		1.46
particle absorption	K	0.001
non-sphericity factor		1
Calibration Standard Parameters		
peak diameter	nm	239
half height peak width	μm	0.027
particle density		1.385
Fluid Parameters		
fluid density	g/mL	1.051

fluid Refractive Index		1.3612
fluid viscosity	cps*	1.28

*cps=centipoise

System configuration

The measurement wavelength was set to 405 nm. The following runtime options parameters were established:

Force Baseline:	Yes
Correct for Non-Stokes:	No
Extra Software Noise Filtration:	No
Baseline Drift Display:	Show
Calibration method:	External
Samples per calibration:	1

All the other options of the software are left as set by the manufacturer of the instrument.

Preparation of the disc centrifuge

The centrifugal disc is rotated at 24000 rpm during 30min. The density gradient of sucrose (CAS n°57-50-1) is prepared as follows:

In a 50mL beaker, a 24% in weight aqueous solution of sucrose is prepared. In a 50mL beaker, a 8% in weight aqueous solution of sucrose is prepared. Once these two solutions are homogenized separately, samples are taken from each solution using a 2 mL syringe which is injected into the rotating disc in the following order:

Sample 1: 1.8 mL of the 24 wt% solution
Sample 2: 1.6 mL of the 24 wt% solution + 0.2 mL of the 8 wt% solution
Sample 3: 1.4 mL of the 24 wt% solution + 0.4 mL of the 8 wt% solution
Sample 4: 1.2 mL of the 24 wt% solution + 0.6 mL of the 8 wt% solution
Sample 5: 1.0 mL of the 24 wt% solution + 0.8 mL of the 8 wt% solution
Sample 6: 0.8 mL of the 24 wt% solution + 1.0 mL of the 8 wt% solution
Sample 7: 0.6 mL of the 24 wt% solution + 1.2 mL of the 8 wt% solution
Sample 8: 0.4 mL of the 24 wt% solution + 1.4 mL of the 8 wt% solution
Sample 9: 0.2 mL of the 24 wt% solution + 1.6 mL of the 8 wt% solution
Sample 10: 1.8 mL of the 8 wt% solution

Before each injection into the disk, the two solutions are homogenized in the syringe by aspiring about 0.2 mL of air followed by brief manual agitation for a few seconds, making sure not to lose any liquid.

These injections, the total volume of which is 18 mL, aim to create a density gradient useful for eliminating certain instabilities which may appear during the injection of the sample to be measured. To protect the density gradient from evaporation, we add 1 mL of dodecane in the rotating disc using a 2 mL syringe. The disc is then left in rotation at 24000 rpm for 60 min before any first measurement.

Sample preparation

3.2 g of silica in a 50mL high shape glass beaker (SCHOTT DURAN: diameter 38 mm, height 70 mm) were weighed and 40 mL of deionized water were added. The suspension was stirred with a magnetic stirrer at 300 rpm (minimum 20 s) before placing the beaker into a crystallizing dish filled with ice and cold water. The magnetic stirrer was removed, and the crystallizing dish was placed under the ultrasonic probe placed at 1 cm beneath the air-liquid interface. The ultrasonic probe was set to 60% of its maximum amplitude and was activated for 8 min. At the end of the sonication the beaker was placed again on the magnetic stirrer with a 2 cm magnetic stir bar stirring at minimum 500 rpm until after the sampling.

The ultrasonic probe should be in proper working conditions. The following checks have to be carried out and in case of negative results a new probe should be used. As is known to those skilled in the art, an acceptable state of wear is usually considered to be a surface state that does not have any visually perceptible roughness. As a reference for an unacceptable state of wear, use may be made, for example, of the right-hand image on figure 3, page 14, published in "Preparation of Nanoparticle Dispersions from Powdered Material Using Ultrasonic Disruption, version 1.1, [J. S. Taurozzi, V. A. Hackley, M. R. Wiesner], National Institute of Standards and Technology Special Publication 1200-2, June 2012" (CODEN NSPUE, publication available using the digital identifier dx.doi.org/10.6028/NIST.SP.1200-2).; the measured d_{50} of commercial silica Zeosil® 1165MP should be 93 nm ± 3 nm.

Analysis

Before each sample was analysed, a calibration standard was recorded. In each case 0.1 mL of the PVC standard provided by CPS Instruments and whose characteristics were previously entered into the software was injected. It is important to start the measurement in the software simultaneously with this first injection of the PVC standard. The confirmation of the device has to be received before injecting 100 µL of the previously sonicated sample by making sure that the measurement is started simultaneously at the injection.

These injections were done with 2 clean syringes of 1 mL.

At the end of the measurement, which is reached at the end of the time necessary to sediment all the particles of smaller diameter (configured in the software at 0.02 µm), the ratio for each diameter class was obtained. The curve obtained is called aggregate size distribution. The integration of the aggregate size distribution as a function of the diameter makes it possible to obtain what is referred to as a "cumulative" distribution; that is to say, the total weight of aggregates between the minimum diameter measured and a diameter of interest.

Results

The values d_{50}, d_{16}, d_{84} and L_d are on the basis of distributions drawn in a linear scale. The integration of the particle size distribution function of the diameter allows obtaining a "cumulative" distribution, that is to say the total mass of particles between the minimum diameter and the diameter of interest.

d_{50}: is the diameter below and above which 50% of the population by mass is found. The d_{50} is called median size, that is diameter, of the silica particle. It is expressed in nm.

d_{84}: is the diameter below which 84% of the total mass of particles is measured. It is expressed in nm.

d_{16}: is the diameter below which 16% of the total mass of particles is measured. It is expressed in nm.

L_d: is calculated according to equation: $L_d=(d_{84}-d_{16})/d_{50}$. L_d is a dimensionless number.

FWHM: is calculated on the derivative curve of the above-mentioned cumulative distribution as explained above in the specification.

Determination of the rate of fines by the "sedigraph" method

In this test, the ability to disperse silica is measured by a particle size measurement (by sedimentation) carried out on a silica suspension previously deagglomerated by ultrasonification. Deagglomeration (or dispersion) under ultrasound is implemented using a VIBRACELL BIOBLOCK sonifier (1500 W), equipped with a probe with a diameter of 19 mm. The particle size measurement is carried out using a SEDIGRAPH particle size meter (sedimentation in the gravity field + X-ray beam scanning).

6.4 grams of silica are weighed in a high form beaker (volume equal to 100 ml) and supplemented to 80 grams by adding permuted water: an aqueous suspension of 8% silica is thus made which is homogenized for 2 minutes by magnetic stirring. Deagglomeration (dispersion) under ultrasound is then carried out as follows: the probe being immersed over a length of 3 cm, the output power is adjusted to deliver 58kJ to the suspension) in 480 seconds. The particle size measurement is then carried out by means of a SEDIGRAPH particle size meter. The measurement is done between 85μm and 0.3μm with a density of 2.1g/mL. The deagglomerated silica suspension, optionally cooled beforehand, is then circulated in the sedigraph particle size cell. The analysis stops automatically as soon as the size of 0.3 μm is reached (about 45 minutes). The fine ratio (τf) is then calculated, i.e. the proportion (by weight) of particles smaller than 1μm in size. The higher this rate of fines (τf) or particles with a size less than 1 μm is, the better the dispersibility of the silica is.

It is understood that the ultrasonic probe should be in proper working conditions. To this end, the following checks can be carried out: (i) visual check of the physical integrity of the end of the probe (depth of roughness less than 2 mm measured with a fine caliper); and/or (ii) the measure of τf commercial silica Zeosil® 1165MP, aged for at least 2 years, should be 97%. In case of negative results, the power output should be re-adjusted. If negative results are persisting, a new probe should be used.

Determination of the primary particles size by SAXS

1) Principle of the method

Small angle X-ray scattering (SAXS) consists of exploiting the deviation of an incident X-ray beam, of wavelength λ, passing through the sample, in a cone of a few degrees of angle. A scattering angle θ corresponds to a wave vector defined by the following relation:

$$q = \frac{4\pi}{\lambda} \sin\frac{\theta}{2}$$

whose unit is $Å^{-1}$.

Each scattering angle corresponds to a wave vector q defined in the reciprocal space. This wave vector corresponds to a spatial scale defined in the real space, and which is equivalent to 2π / q. Scattering at small angles therefore characterizes large distances in the sample, and conversely scattering at large angles characterizes small distances in the sample. The technique is sensitive to the way matter is distributed in space.

Basic references on this technique are given below:

[1] Small Angle Scattering of X rays, Guinier A., Fournet G., (1955), Wiley, New 5 York.

[2] Small Angle X Ray Scattering, Glatter O., Krattky O., (1982), Academic Press, New York.

[3] Analysis of the Small-Angle Intensity Scattered by a Porous and Granular Medium, Spalla O., Lyonnard S., Testard F., J. Appl. Cryst. (2003), 36, 338-347. 10

The requirements for SAXS to characterize silica according to the following criterion are as follows:

- SAXS assembly working in a transmission geometry (i.e. the incident beam passing through the sample), with an incident wavelength between 0.5 and 2 Angströms (Å),
- wave vector interval q between 0.015 $Å^{-1}$ and 0.30 $Å^{-1}$, which makes it possible to characterize distances in the real space ranging from 420 to 20 Å,
- assembly verified in q scale using a suitable standard (e.g. silver behenate, octadecanol or any other compound giving a fine SAXS line included in the interval of q above),
- one-dimensional linear detector or preferably two-dimensional,
- the assembly must make it possible to measure the transmission of the preparation, i.e. the ratio between the intensity transmitted by the sample and the incident intensity.

Such an assembly may be for example a laboratory assembly, operating on a source of type X-ray tube or rotating anode, preferably using Kα emission of copper at 1.54 Å. The detector can be a CCD detector, an image plate or a gas detector. It can also be a SAXS mount on synchrotron. In the frame of the present application, a CCD detector was used.

2) Procedure:

The silica sample is analyzed in powdery solid form. The powder is placed between two transparent windows with X-rays. Independently of this preparation, an empty cell is made with only two transparent windows, without silica inside. Diffusion by the empty cell shall be recorded separately from silica diffusion. During this operation, called "background measurement", the scattered intensity comes from all external contributions to silica, such as electronic background noise, diffusion through transparent windows, residual divergence of the incident beam.

These transparent windows must provide a low background noise in front of the intensity scattered by the silica over the wave vector interval explored. They may consist of mica, Kapton or mylar film, or preferably adhesive Kapton film or mylar with a thin grease layer.

Prior to the actual SAXS acquisition of silica, the quality of the preparation must be checked by means of the transmission measurement of the silica-laden cell.

The steps to be taken are therefore as follows:

2.1) Elaboration of a cell consisting of two silica-free windows (empty cell).

2.2) Elaboration of a cell consisting of two windows, with a sample of silica powder inside.

The amount of silica introduced should be less than 50 mg. The silica must form a layer of thickness less than 100 μm. Preference is given to obtain a monolayer of silica grains arranged on a window, which is easier to obtain with adhesive windows. The quality of the preparation is controlled by the measurement of transmission (step 2.3)).

2.3) Measurement of the transmission of the empty cell and the silica cell.

The R ratio is defined as follows:
R = transmission of silica cell / transmission of empty cell

R should be between 0.85 and 1, in order to minimize the risk of multiple scattering, while maintaining a signal-to-noise ratio satisfactory to large q. If the R-value is too low, the amount of silica visible to the beam should be reduced; if it is too high, silica must be added.

2.4) SAXS acquisition on the empty cell and on the silica cell.

The acquisition times shall be determined in such a way that the signal-to-noise ratio at large q is acceptable. They shall be such that in the immediate vicinity of $q = 0, 12$ $Å^{-1}$, the fluctuations of the function F(q) defined below shall not exceed +/- 5% with respect to the value taken by the function F at that point.

2.5) If a two-dimensional detector has been used: radial grouping of each of the two two-dimensional profiles to obtain the scattered intensity as a function of the wave vector q. The determination of the scattered intensity must take into account the exposure time, the intensity of the incident beam, the transmission of the sample, the solid angle intercepted by the detector pixel. The determination of the wave vector shall take into account the wavelength of the incident beam and the sample-detector distance.

2.6) If a single-dimensional detector has been used: the previous determinations concerning the scattered intensity and the wave vector are to be made, but there is no radial grouping to be expected.

2.7) This leads to two profiles reducing the information to the variation of the scattered intensity as a function of the wave vector q: one profile for the empty cell and one profile for the silica cell.

2.8) Subtraction of the intensity diffused by the empty cell from the intensity scattered by the silica cell (subtraction of "background").

2.9) The SAXS profile of silica, after subtraction of "background", has a monotonous decay which is done according to a regime close to the Porod regime, that is to say that the intensity decreases very quickly with the wave vector according to a law close to a power law in q^{-4}. Small deviations from this Porod law are best visible by representing the data according to the so-called Krattky-Porod method. It is a question of representing F(q) as a function of q, with:

$$F(q) = I \times q^4$$

wherein F represents a SAXS profile in accordance with Kratty-Porod method, I represents the scattered intensity after subtraction of the "background" and q represents the wave vector (in $Å^{-1}$).

2.10) In the Krattky-Porod representation, when describing the profile, one can possibly observe a maximum, which is related to the existence of primary particles of a roughly defined size. The maximum is all the more marked as the polydispersity is low. In the case of monodispersed primary particles, a second or even a third oscillation to the right of the maximum is observed. The position of the maximum is related to the average size of primary particle by a law in $2\pi/q$.

Two different determinations can be carried out, both providing information on the dimensions of the primary particles.

A first determination is based on the position of the maximum in $I \times q^4 = F(q)$. It corresponds to a spatial scale, given by $2\pi / q_{max}$. In the case of a single-strip population of spheres, this distance does not correspond exactly to the diameter but to 115% of the diameter (in Å). This exploitation does not give access to a size distribution, but only to an average diameter in which the largest particles have a strong influence.

Another determination provides the average size d_{ZS} (Zimm Schultz average diameter) in accordance with the present invention. Accordingly, a SAXS profile in I x q^4 = F(q) is modelled by a distribution of independent spheres (having different diameters), of type Zimm-Schultz distribution.

The skilled person is well familiar with the use of such a distribution to fit lots of distributions observed in various fields of Chemistry. As reference articles, it can be notably cited:

- J. Welch, V.A. Bloomfield, J. Pol. Sci., Polymer Physics Edition, vol. 11 (1973), entitled "Fitting Polymer Distribution Data to a Schulz-Zimm Function"

- H.J. Angerman, G. ten Brinke, J.J.M. Slot, The European Physical Journal B, 12, 397-404 (1999), entitled "Influence of polydispersity on the phase behaviour of statistical multiblock copolymers with Schultz-Zimm block molecular weight distributions", and

- L. H. Hanus, H. J. Ploehn, Langmuir, 15, 3091-3100 (1999), entitled "Conversion of Intensity-averaged Photon Correlation Spectroscopy Measurements to Number-Averaged Particle Size Distributions. 1. Theoretical Development".

This last paper relates to the determination of an average particle diameter of a distribution of particles, as it is the case for the inventive silica. Zimm-Schultz distribution function, as shown in Table 1 of this last paper, was evaluated, and general expressions for converting the intensity-average particle diameter and the polydispersity index to the mean and standard deviation of Zimm-Schultz distribution function can be found in Table 2 of this last paper.

The modelled SAXS profile is based on the well-known SAXS shape factor. Accordingly, for one sphere having a diameter d (d = 2 x r, wherein r is the sphere radius, in Å), we have:

$$I(q,r) = \frac{k \times V^2 \times [\sin(q \times r) - q \times r \times \cos(q \times r)]^2}{q^6 \times r^6} \qquad \text{[equation (SF)]}$$

wherein I(q,r) is the scattered intensity of the sphere of diameter d at wave vector q (in $Å^{-1}$), k is a multiplicative constant, V is the sphere volume [i.e. $V = {}^{4}/_{3} \times \pi \times r^3$] and sin and cos denote respectively sinus and cosinus functions.

For a distribution of independent spheres having different diameters, the (total) scattered intensity I(q) after subtraction of the "background" at wave vector q is

$$I(q) = \int_0^{\infty} f(r) \times I(q,r)\, dr$$

wherein f(r) is the distribution function of the independent spheres, and I(q,r), r and q are as previously defined ; the corresponding SAXS profile F(q) is:

$$F(q) = q^4 \times I(q) = q^4 \times \int_0^{\infty} f(r) \times I(q,r)\, dr$$

Zimm Schultz distribution function of independent spheres f(r) = $f_{ZS}(r)$ is commonly represented by:

$$f_{ZS}(r) = \frac{a^{t+1} \times r^t \times \exp(-a \times r)}{\Gamma(t+1)}$$

wherein exp denotes exponential function, Γ denotes gamma function, r is the sphere radius, and t and a are two parameters which are linked to the average diameter d_{ZS} (in Å) and to the dimensionless polydispersity index i_P by the following equations:

$$t = \frac{1}{i_P^2} - 1 \qquad\qquad a = \frac{2 \times (t+1)}{d_{ZS}}$$

The modelled SAXS profile based on independent spheres having a Zimm-Schultz distribution in accordance with the invention $F_{ZS}(q)$ is thus:

$$F_{ZS}(q) = k \times q^4 \times \int_0^{\infty} \frac{a^{t+1} \times r^t \times \exp(-a \times r) \times V^2 \times [\sin(q \times r) - q \times r \times \cos(q \times r)]^2}{\Gamma(t+1) \times q^6 \times r^6}\, dr$$

wherein q (in $Å^{-1}$), r (in Å), V (in $Å^3$), k, a and t are as previously defined, and wherein exp, Γ, sin and cos denote the same functions as above specified.

Thus, the modelled profile needs two inputs to be fitted: 1) average diameter d_{ZS} and 2) polydispersity index i_P (through parameters t and a).

In addition, multiplicative constant k is used to adjust F_{ZS} profile in the y axis.

These inputs can be determined using conventional numerical tools or on a trial and error basis, in order to best match $F(q) = I.q^4$ (SAXS profile in Krattky-Porod's representation) inside a wave vector interval [q_{min}, q_{max}] which must include the wave vector point at which F(q) reaches its maximum (for the avoidance of doubt, q_{min} and q_{max}, expressed in $Å^{-1}$, denote respectively the lower and upper bounds of the wave vector interval). The best fit will be found when the modelled data and the experimental data match as closely as possible in the interval surrounding the maximum (that is to say when the sum of the differences between the squares of the experimental values for F(q) and the modelled values $F_{ZS}(q)$ is minimum).

In practice, Zimm-Schultz distribution is discretized into classes inside a selected radius interval [r_{min}, r_{max}]. At a given wave vector, each class of discretized Zimm Schultz distribution contributes to the modelled SAXS profile $F_{ZS}(q)$ through its shape factor [I(q,r), equation (SF)] and its weight $f_{ZS}(r)$:

$$F_{ZS}(q) = q^4 \times I_{ZS}(q)$$

$$I_{ZS}(q) = \sum_{r_{min}}^{r_{max}} f_{ZS}(r) \times I(q,r)\,dr$$

wherein $F_{ZS}(q)$ is the modelled SAXS profile, $I_{ZS}(q)$ is the modelled scattered intensity, $f_{ZS}(r)$ is Zimm Schultz distribution function, I(q,r) is the scattered intensity of a sphere, q is the wave vector, r is the sphere radius and r_{min} and r_{max} are the lower and upper bounds of the selected interval for the sphere radius. The selected interval shall include Zimm Schultz average radius r_{ZS} ($r_{ZS} = d_{ZS}/2$). Typically, a skilled person may select for r_{min} a value close to expected $r_{ZS}/20$ ($r^{\circ}_{ZS}/20$, with r°_{ZS} as defined below) and define 50 values which follow a geometric progression with a ratio of 1.1. Other choices are possible as long as the diameter distribution is correctly taken into account in the modelled profile. The choice of initial values for the determination of r_{ZS} and i_P (respectively, r°_{ZS} and i°_{P}) as starting point for an iterative determination process is not especially critical. A skilled person may e.g. advantageously use $r^{\circ}_{ZS} = 40$ Å and $i_P = 0.50$ as starting values; these ones are especially suitable for the silicas in accordance with the present invention. Alternatively, or complementarily, the skilled person may rely on TEM measurements.

For convenience, the calculations may be made after introducing the above formulae in a spreadsheet.

This model does not take into account aggregation, therefore the existence of correlations between spheres; it also does not take into account consolidation, i.e. the presence of additional material that welds the primary particles.

2.11) From Zimm-Schultz distribution model, we determine the SAXS particle size which is an average diameter d_{ZS} (Zimm-Schultz' average diameter).

Measurement of the amount of aluminium (W_{Al})

The weight amount of aluminium, based on the weight amount of SiO_2, was measured using XRF wavelength dispersive X-ray fluorescence spectrometry using a WDXRF Panalytical instrument. Sample analyses were performed under helium in a 4 cm diameter cell using silica, especially silica powder, contained in the cell covered by a thin Prolene film (4 µm Chemplex®) over a range Al/SiO_2 of from 0.1 to 3.0% (in weight).

Al and Si fluorescence were measured using the following parameters: Al Kα angle 2θ = 144.9468° (20 s), background signal angle 2θ = -1.2030° (4s), Si Kα angle 2θ = 109.1152° (10 s), tube power 4 kW (32 kV, 125 mA), PE002 crystal and 550 µm collimator, gas flux detector.

Glass transition temperature Tg

The glass transition temperature Tg is measured in a known way by DSC (Differential Scanning Calorimetry) according to standard ASTM D3418, 2008

Microstructure of the elastomer

Near-infrared spectroscopy (NIR) is used to quantitatively determine the content by weight of styrene in the elastomer and its microstructure (relative distribution of the 1,2-vinyl-, trans-1,4- and cis-1,4- butadiene units). The principle of the method is based on the Beer-Lambert law generalized for a multicomponent system. As the method is indirect, it involves a multivariate calibration [Vilmin, F., Dussap, C. and Coste, N., Applied Spectroscopy, 2006, 60, 619-29] performed using standard elastomers having a composition determined by ^{13}C NMR. The styrene content and the microstructure are then calculated from the NIR spectrum of an elastomer film having a thickness of approximately 730 µm. The spectrum is acquired in transmission mode between 4000 and 6200 cm^{-1} with a resolution of 2 cm^{-1} using a Bruker Tensor 37 Fourier-transform near-infrared spectrometer equipped with an InGaAs detector cooled by the Peltier effect

Tensile tests

The tensile tests make it possible to determine the breaking properties; those carried out on the cured mixtures in accordance with the standard NF ISO 37 of December 2005. The tensile strength, in MPa, and the deformation at break, in%, are measured at 23 °C ± 2° C., and under normal humidity conditions (50 ± 5% relative humidity), according to French Standard NF T 40-101 (December 1979).

For greater legibility in the presentation of the results below and facilitated comparison, the results are given in base 100, the value 100 being fixed for the control. A result greater than 100 in terms of tensile strength or in terms of deformation at break indicates an increased value and therefore an improved performance in terms of tensile strength or in terms of deformation at break, for the composition compared with the control.

Dynamic properties of the tire elastomeric compositions (after curing)

The dynamic properties G* and tan(δ) are measured on a viscoanalyzer (Metravib VA4000), according to standard ASTM D5992-96. The response of a sample of vulcanized composition (cylindrical test piece 4 mm thick and 10 mm in diameter) subjected to a sinusoidal stress in simple alternating shear, at a frequency of 10 Hz, during a sweep is recorded. in temperature from -80°C to +100°C with a ramp of +1.5°C/min, under a maximum stress of 0.7 MPa. The value of the tangent of the loss angle (tan delta or tan(δ)) is then plotted at 0°. The value of the dynamic modulus G* is raised at 60°C. The results used are therefore the values of tan(δ) at 0°C and the complex dynamic shear modulus G* at 60°C obtained on the temperature scan at 0.7 MPa.

The results of tan(δ) at 0°C are expressed in terms of performance in base 100, i.e. the value 100 is arbitrarily assigned to the control, in order to consecutively compare the tan(δ) at 0° C (i.e. wet grip) of the various sample compositions tested. The value in base 100 of the sample composition tested is calculated according to the operation: (value of tan(δ) at 0°C of the sample / value tan(δ) at 0°C of the control) × 100. A result greater than 100 indicates improved performance, that is to say that the composition of the sample considered has better grip on wet ground compared to the control composition.

The results of G* at 60°C are expressed in terms of performance in base 100, i.e. the value 100 is arbitrarily assigned to the control, in order to consecutively compare the G* at 60°C (i.e. the stiffness and, therefore, the handling) of the different sample compositions tested. The value in base 100 of the sample composition tested is calculated according to the operation: (value of G* at 60°C of the sample / value G* at 60°C of the control) × 100. Therefore, a score greater than 100 indicates improved performance, i.e. improved stiffness.

The dynamic property tan(δ)max at 23° C. are measured on a viscoanalyzer (Metravib VA4000), according to standard ASTM D5992-96. The response of a sample of vulcanized composition (cylindrical specimen 4 mm thick and 10 mm in diameter) subjected to a sinusoidal stress in alternating simple shear, at a frequency of 10 Hz, under normal temperature conditions, is recorded. 23°C according to ASTM D 1349-09. A deformation amplitude scan is performed from 0.1% to 100% (go cycle), then from 100% to 0.1% (return cycle). The result used is the maximum of the tangent of the loss angle tan(δ) at 23°C on the return cycle, noted tan(δ)max at 23°C.

The results of tan(δ)max at 23°C are expressed in terms of performance in base 100, i.e. the value 100 is arbitrarily assigned to the control, in order to consecutively compare the tan(δ)max to 23°C (i.e. the hysteresis properties) of the various sample compositions tested. The value in base 100 for the sample is calculated according to the operation: (value of tan(δ)max at 23°C of the control / value tan(δ)max at 23°C of the sample) × 100. A result greater than 100 indicates improved performance, that is to say that the composition of the sample under consideration exhibits improved hysteretic properties corroborating better rolling resistance compared to the control elastomeric composition.

EXAMPLES

Examples 1 to 4: synthesis of silica

Example 1- Comparative Silica 1 (SC1)

The comparative silica, Zeozil 1165MP, is commercialized by Solvay

The properties of the precipitated silica SC1 are reported in Table I.

Example 2- Comparative Silica 2 (SC2)

In a 2500L stainless steel reactor were introduced 1126 L of water and 29.7 kg of Na_2SO_4 (solid). The obtained solution was stirred and heated to reach 92°C. The entire reaction was carried out at this temperature. A 96 wt% sulfuric acid solution was introduced into the reactor to reach a pH value of 3.90. A sodium silicate solution (SiO_2/Na_2O ratio = 3.45; SiO_2 concentration = 19.3wt%) at a flowrate of 420 L/h was introduced in the reactor over a period of 51 s. The same sodium silicate solution was used throughout the process. Next a sodium silicate solution at a flowrate of 445 L/h, a water flowrate of 575 L/h and a 96 wt% sulfuric acid solution were simultaneously introduced over 14.9 min period. The flowrate of sulfuric acid was regulated so that the pH of the reaction medium was maintained at a value of 4.30. At the end of this step, sodium silicate at a flowrate of 445 L/h and a 96 wt% sulfuric acid solution were introduced simultaneously over a period of 9.45 min. The 96 wt% sulfuric acid solution flowrate was regulated so that the pH of the reaction medium was maintained at a value of 4.30.

The introduction of acid was then stopped while the addition of sodium silicate was put at the flowrate of 579 L/h until the reaction medium reached the pH value of 8.00.

Sodium silicate at a flowrate of 708 L/h and a 96 wt% sulfuric acid solution were then introduced simultaneously over a period of 3 min. The flowrate of the 96 wt% sulfuric acid solution was regulated so that the pH of the reaction medium was maintained at a value of 8.00.

Simultaneously, over a period of 14.8 min, were introduced: sodium silicate, at a flowrate of 706 l/h, a sodium aluminate solution (weight % Al: 12.2% - weight Na_2O: 19.4%), at a flowrate of 47.6 kg/h and a 96% sulfuric acid solution. The flowrate of the 96% sulfuric acid solution was regulated so that the pH of the reaction medium was maintained at a value of 8.00.

At the end of this simultaneous addition, the pH of the reaction medium was brought to a value of 4.40 with 96 wt% sulfuric acid. Then water is introduced to decrease the temperature to 85°C and the reaction mixture was matured for 5 minutes. A slurry was obtained.

The reaction slurry was filtered and washed on a filter press to give a precipitated silica cake with a solid content of 23% by weight.

Silica cake obtained was then subjected to a liquefaction step in a continuous vigorously stirred reactor. 200g of 7.7% sulfuric acid solution was then add to the mix to adjust the pH. The pH value of the liquefied cake was 6.0 and a solid content of 23% by weight

The resulting slurry was dried by means of a nozzle spray dryer and then granulated to obtained precipitated silica SC2.

The properties of the precipitated silica SC2 are reported in Table I.

Example 3-Silica S1

In a 2500L stainless steel reactor were introduced 1124 L of water and 29.7 kg of Na_2SO4 (solid). The obtained solution was stirred and heated to reach 92°C. The entire reaction was carried out at this temperature.

A sodium silicate solution (SiO_2/Na_2O ratio = 3.45; SiO_2 concentration = 19.3wt%) at a flowrate of 445 L/h, a water flowrate of 575 L/h and a 96 wt% sulfuric acid solution were simultaneously introduced over 3.7 min period. The flowrate of sulfuric acid was regulated so that the pH of the reaction medium was maintained at a value of 8.2.

The introduction of sodium silicate was then stopped until the reaction medium reached the pH value of 4.00.

Next a sodium silicate solution at a flowrate of 445 L/h, a water flowrate of 575 L/h and a 96 wt% sulfuric acid solution were simultaneously introduced over 9.8 min period. The flowrate of sulfuric acid was regulated so that the pH of the reaction medium was maintained at a value of 4.00. At the end of this step, sodium silicate at a flowrate of 445 L/h and a 96 wt% sulfuric acid solution were introduced simultaneously over a period of 5.9 min. The 96 wt% sulfuric acid solution flowrate was regulated so that the pH of the reaction medium was maintained at a value of 4.00.

The introduction of acid was then stopped while the addition of sodium silicate was put at the flowrate of 610 L/h until the reaction medium reached the pH value of 8.00.

Sodium silicate at a flowrate of 705 L/h and a 96 wt% sulfuric acid solution were then introduced simultaneously over a period of 22.4 min. The flowrate of the 96 wt% sulfuric acid solution was regulated so that the pH of the reaction medium was maintained at a value of 8.00.

At the end of this simultaneous addition, the pH of the reaction medium was brought to a value of 4.80 with 96 wt% sulfuric acid. Then water is introduced to decrease the temperature to 85°C and the reaction mixture was matured for 5 minutes. A slurry was obtained.

Each reaction slurry was filtered and washed on a filter press to give a precipitated silica cake with a solid content of 23% by weight.

Silica cake obtained was then subjected to a liquefaction step in a continuous vigorously stirred reactor with addition of a sodium aluminate solution ([Al]: 12.5wt% - [Na_2O]: 19.5wt%) and sulfuric acid solution at 7.7% by mass to adjust the pH. The quantity of sodium aluminate solution is added to target a ratio %Al/SiO_2 of 0.55%. The pH value of the liquefied cake was 6.40 and a solid content of 23% by weight.

The resulting slurry was dried by means of a nozzle spray dryer to obtain precipitated silica S1.

The properties of the precipitated silica S1 are reported in Table I.

Example 4-Silica S2

In a 2500L stainless steel reactor were introduced 1124 L of water and 29.7 kg of Na_2SO_4 (solid). The obtained solution was stirred and heated to reach 92°C. The entire reaction was carried out at this temperature.

A sodium silicate solution (SiO_2/Na_2O ratio = 3.45; SiO_2 concentration = 19.3wt%) at a flowrate of 445 L/h, a water flowrate of 575 L/h and a 96 wt% sulfuric acid solution were simultaneously introduced over 6.2 min period. The flowrate of sulfuric acid was regulated so that the pH of the reaction medium was maintained at a value of 8.2.

The introduction of sodium silicate was then stopped until the reaction medium reached the pH value of 4.0.

Next a sodium silicate solution at a flowrate of 445 L/h, a water flowrate of 575 L/h and a 96 wt% sulfuric acid solution were simultaneously introduced over 7.1 min period. The flowrate of sulfuric acid was regulated so that the pH of the reaction medium was maintained at a value of 3.85. At the end of this step, sodium silicate at a flowrate of 445 L/h and a 96 wt% sulfuric acid solution were introduced simultaneously over a period of 6 min. The 96 wt% sulfuric acid solution flowrate was regulated so that the pH of the reaction medium was maintained at a value of 3.85.

The introduction of acid was then stopped while the addition of sodium silicate was put at the flowrate of 610 L/h until the reaction medium reached the pH value of 8.00.

Sodium silicate at a flowrate of 705 L/h and a 96 wt% sulfuric acid solution were then introduced simultaneously over a period of 22.4 min. The flowrate of the 96 wt% sulfuric acid solution was regulated so that the pH of the reaction medium was maintained at a value of 8.00.

At the end of this simultaneous addition, the pH of the reaction medium was brought to a value of 4.80 with 96 wt% sulfuric acid. Then water is introduced to decrease the temperature to 85°C and the reaction mixture was matured for 5 minutes. A slurry was obtained.

Each reaction slurry was filtered and washed on a filter press to give a precipitated silica cake with a solid content of 23% by weight.

Silica cake obtained was then subjected to a liquefaction step in a continuous vigorously stirred reactor with addition of a sodium aluminate solution ([Al]: 12.5wt% - [Na_2O]: 19.5wt%) and sulfuric acid solution at 7.7% by mass to adjust the pH. The quantity of sodium aluminate solution is added to target a ratio %Al/SiO_2 of 0.55%. The pH value of the liquefied cake was 6.4 and a solid content of 23% by weight.

The resulting slurry was dried by means of a nozzle spray dryer to obtain precipitated silica S2. The properties of the precipitated silica S2 are reported in Table I.

Table I

Products	CTAB (m^2/g)	BET (m^2/g)	W_{Al} (wt%)	d_{50} (nm)	d_{84} (nm)	FWHM (nm)	L_d	τf (%)	relation FWHM: -0.16 ×|CTAB| + 130	AS0 silicate ratio (%)	Primary particles size d_{zs} (nm)
SC1	155	160	0.33	93	175	65	1.3	98	105	n.c	15.1
SC2	158	208	1.39	146	336	131	1.8	88	105	0.0	7.2
S1	162	180	0.52	135	309	124	1.8	99	104	6.1	8.3
S2	161	177	0.56	138	301	136	1.7	99	104	9.9	8.1

n.c: not communicated

EXAMPLE 5 : use of silica in elastomeric compositions

The following tables II and IV give the formulation of the different compositions; the contents being expressed as phr (parts by weight per hundred parts by weight of elastomers).

The optimal content of diphenylguanidine (DPG) is adapted depending on the BET specific surface area of the silica to be tested.

Indeed, the greater the BET specific surface area of a silica, the more it is necessary to use a high content of DPG to cover the surface of the silica and promote the dispersion thereof. Those skilled in the art know how to adapt these contents depending on the nature of the silica used. The formulations may be compared.

The optimal content of coupling agent between the silica and the elastomers is adapted depending on the CTAB surface area of the silica to be tested.

Indeed, the greater the CTAB specific surface area of silica, the more it is necessary to use a high content of coupling agent between the silica and the elastomers in order to maintain an equivalent amount of elastomer/silica bonds per unit of silica surface area. Those skilled in the art know how to adapt these contents depending on the nature of the silica used. The formulations may be compared.

The total amount of sulfur in the elastomeric compositions is the same in all the compositions. Said total amount of sulfur is the sum of the amount of the sulfur added into the composition (Sol Sulfur 2H) and the amount of the sulfur which is release by the coupling agent between the silica and the elastomers during the manufacture of the composition.

The compromise of the five properties which are rigidity, grip on wet ground, tensile strength at 23°C, deformation at break at 23°C and rolling resistance can be obtained by calculating the arithmetic mean of results presented in base 100.

The elastomeric compositions to be tested are prepared in the following way: : the diene elastomers, then silica to be tested, the agent for coupling the elastomer to the silica, and then, after kneading for one to two minutes, the various other ingredients, with the exception of the sulfur and the sulfenamide primary accelerator, are introduced into an internal mixer which is 72% filled and which has an initial vessel temperature of approximately 70°C. Thermomechanical working is then carried out (non-productive phase) in one or two steps (total duration of the kneading equal to approximately 3 to 5 min, until a maximum "dropping" temperature of approximately 165-170°C is reached. The mixture thus obtained is recovered and cooled and then the sulfur and sulfenamide accelerator are added on an external mixer (homofinisher) at 70°C, everything being mixed (productive phase) for 11 to 12 minutes.

The compositions are then formed for the measurements of their physical or mechanical properties (for example in the form of 4 mm test specimens, etc.) and where appropriate are cured (or vulcanized) for the measurements of the cured properties.

Test A

The aim of this test is to demonstrate that the compromise of properties is improved for the tire elastomeric compositions in accordance with the invention (compositions C1 and C2), based on inventive precipitated silicas, compared to a tire elastomeric composition conventionally used and sold in “green tyres” (composition T1) and a tire elastomeric composition comprising a silica of the state of the art (composition T2).

Table II gives the formulation of the different compositions, the contents being expressed as phr (parts by weight per hundred parts by weight of elastomers).

The control tire elastomeric composition T1 is representative of elastomeric compositions used in commercial “green tyres”, which are known to have good mechanical properties. Said control composition comprises the Zeosil 1165 MP silica sold by the company Solvay.

Table II

	T1	T2	C1	C2
Elastomer (1)	60.00	60.00	60.00	60.00
Elastomer (2)	40.00	40.00	40.00	40.00
Silica SC1	100.00			
Silica SC2	(-)	100.00	(-)	(-)
Silica S1	(-)	(-)	100.00	(-)
Silica S2	(-)	(-)	(-)	100.00
Carbon black (3)	3.00	3.00	3.00	3.00
Plasticizer (4)	9.00	5.00	5.00	5.00
Plasticizer (5)	45.60	50.80	50.80	50.80
TMQ (6)	1.40	1.40	1.40	1.40

Antiozone wax (7)	2.25	2.25	2.25	2.25
Antioxydant (8)	3.40	3.40	3.40	3.40
Coupling agent (9)	8.10	8.67	8.83	8.78
DPG (10)	2.00	2.94	2.52	2.48
Stearic acid	3.00	3.00	3.00	3.00
ZnO	1.50	1.50	1.50	1.50
Accelerator (11)	2.30	2.30	2.30	2.30
Sol Sulfur 2H	1.00	0.94	0.92	0.93

(1) Elastomer: Styrene/butadiene copolymer SBR, having a tertiary amine-alkoxysilane function in the middle of the chain and having a glass transition temperature, measured according to standard D3418 of 2008, equal to -65°C. Its microstructure, determined by the NIR method, is as follows: the content by weight of 1,4-trans units is 48%, that of 1,4-cis units is 28% and that of 1,2- units is 24% (each of these three contents relates to the butadiene units). The content by weight of styrene units is 15% by weight relative to the total weight of the elastomer.

(2) Elastomer: Styrene/butadiene copolymer SBR, having a tertiary amine-alkoxysilane function in the middle of the chain and having a glass transition temperature, measured according to standard D3418 of 2008, equal to -48°C. Its microstructure, determined by the NIR method, is as follows: the content by weight of 1,4-trans units is 48%, that of 1,4-cis units is 28% and that of 1,2- units is 24% (each of these three contents relates to the butadiene units). The content by weight of styrene units is 24.5% by weight relative to the total weight of the elastomer.

(3) Carbon black: Carbon black grade N234 according to ASTM standard D1765-14.

(4) Plasticizer: Sunflower oil comprising 85% by weight of oleic acid, sold by Novance under the reference “Lubrirob Tod 1880”;

(5) Plasticizer: DCDP resin sold by Exxon under the reference ECR-383, said resin having a softening point of 100°C and a Tg a glass transition temperature, measured according to standard D3418 of 2008, equal to 51°C and a polydispersity index of 1.65.

(6) TMQ : 2,2,4-trimethyl-1,2-dihydroquinoline sold by Flexys(4)

(7) Anti-ozone wax "Varazon 4959" from Sasol

(8) Antioxidant: N-(1,3-dimethylbutyl)-N-phenyl-para-phenylenediamine sold by Flexsys under the reference Santoflex 6-PPD;

(9) Coupling agent: Bis[3-(triethoxysilyl)propyl] tetrasulfide silane (TESPT) sold by Evonik under the reference Si69;

(10) DPG: diphenylguanidine, sold by Flexsys under the reference Perkacit;

(11) Accelerator: N-cyclohexyl-2-benzothiazolesulfenamide sold by Flexsys under the reference Santocure CBS.

The amount of the plasticizing agent (here the oil and the resin) has been adapted in order that the compositions have the same rigidity.

The properties of said compositions are measured after curing at 150°C for 40 min are reported in table III.

Table III

	T1	T2	C1	C2
G* 60°C base 100	100	103	98	101
Tan(δ)max at 23°C (base 100)	100	135	121	121
Tan(δ)max at 0°C (base 100)	100	104	108	105
Tensile strength at 23°C (base 100)	100	87	98	97
Deformation at break at 23°C (base 100)	100	79	93	94
Properties compromise	100	102	107	107
note Z	43	62	55	56

Compared to the control tire elastomeric composition T1, the tire elastomeric compositions C1 and C2 of the present invention have surprisingly an improved grip on wet ground (tan(δ)max 0°C) and improved rolling resistance (tan (δ) max at 23°C), and comparable rigidity properties (G* 60°C) and comparable deformation and the tensile strength properties.

Compared to the control tire elastomeric composition T2, the tire elastomeric compositions C1 and C2 of the present invention have surprisingly an improved grip on wet ground and improved deformation and the tensile strength properties for comparable rigidity properties.

Surprisingly, the elastomeric compositions C1 and C2 of the present invention have the best compromise of properties: rigidity/ grip on wet ground / rolling resistance/ deformation and the tensile strength properties.

The inventive precipitated silica used in the elastomeric compositions C1 and C2 of the present invention have an improved dispersibility compared to the precipitated silica used in the control elastomeric composition T1.

Test B

The aim of this test is to demonstrate that the compromise of properties is improved for the tire elastomeric compositions in accordance with the invention (compositions C4 to C7), based on other inventive precipitated silicas, compared to a tire elastomeric composition comprising a silica conventionally used and sold in “green tyres” (compositions T5 and T7) and a tire elastomeric composition of the state of the art (compositions T6 and T8).

Table IV gives the formulation of the different compositions; the contents being expressed as phr (parts by weight per hundred parts by weight of elastomers).

Table IV

	T5	T6	C4	C5	T7	T8	C6	C7
Elastomer (1)	60.00	60.00	60.00	60.00	60.00	60.00	60.00	60.00
Elastomer (2)	40.00	40.00	40.00	40.00	40.00	40.00	40.00	40.00
Silica SC1	76.00	(-)	(-)	(-)	130.00	(-)	(-)	(-)
Silica SC2	(-)	76.00	(-)	(-)	(-)	130.00	(-)	100
Silica S1	(-)	(-)	76.00	(-)	(-)	(-)	130.00	(-)
Silica S2	(-)	(-)	(-)	76.00	(-)	(-)	(-)	130.00
Carbon black (3)	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Plasticizer (4)	2.00	(-)	(-)	(-)	29.50	16.60	16.60	16.60

Plasticizer (5)	42.50	45.00	45.00	45.00	40.50	53.80	53.80	53.80
TMQ (6)	1.40	1.40	1.40	1.40	1.40	1.40	1.40	1.40
Antiozone wax (7)	2.25	2.25	2.25	2.25	2.25	2.25	2.25	2.25
Antioxydant (8)	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Coupling agent (9)	6.16	6.59	6.71	6.67	10.53	11.28	11.48	11.41
DPG (10)	1.52	2.23	1.92	1.88	2.60	3.82	3.28	3.22
Stearic acid	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
ZnO	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Accelerator (11)	2.30	2.30	2.30	2.30	2.30	2.30	2.30	2.30
Sulfur Sol Sulfur 2H	1.00	0.95	0.94	0.94	1.00	0.93	0.90	0.92

The properties of said compositions are measured after curing at 150°C for 40 min are reported in table V.

Table V

	T5	T6	C4	C5	T7	T8	C6	C7
G* 60°C base 100	100	100	113	111	100	104	110	112
Tan(δ)max at 23°C (base 100)	100	111	106	106	100	143	122	113
Tan(δ)max at 0°C (base 100)	100	103	104	101	100	118	126	132
Tensile strength at 23°C (base 100)	100	90	101	100	100	88	99	105
Deformation at break at 23°C (base 100)	100	82	89	90	100	73	84	88
Properties compromise	100	97	103	102	100	105	108	110

The tire elastomeric compositions C4 to C7 of the present invention comprising the inventive precipitated silica as described above have improved rigidity properties, improved grip on wet ground properties, and improved rolling resistance compared to the control elastomeric compositions T5 and T7.

The tire elastomeric compositions C4 to C7 have improved tensile strength at 23°C, deformation at break at 23°C, and have same or improved grip on wet properties compared to the tire control elastomeric compositions T6 and T8.

CLAIMS

1. A tire elastomeric composition based on at least one elastomer, at least one reinforcing filler comprising at least one precipitated silica, at least one coupling agent between the elastomer and the precipitated silica and at least one crosslinking system, said precipitated being silica characterised by:

- a CTAB surface area in the range from 40 to 525 m^2/g;
- primary particles having an average size d_{ZS} measured by SAXS below 15 nm;
- an amount of aluminium W_{Al} of at least 0.5wt%,
- a rate of fines τf, that is to say a proportion (by weight) of particles of a size less than $1 \mu m$ after deagglomeration by ultrasounds, which is of at least 91%; and
- a particle size distribution measured by centrifugal sedimentation using a CPS, such that for a given value of the CTAB surface area, parameter FWHM is defined by relation (I):

$$| FWHM | > -0.16 \times | CTAB | + 130 \qquad (I)$$

2. The tire elastomeric composition according to claim 1, wherein the precipitated silica has a CTAB surface area from 50 to 300 m^2/g, preferably from 70 to 300 m^2/g, more preferably from 80 to 270 m^2/g or alternatively, from 120 to 275 m^2/g, more preferably from 120 to 230 m^2/g.

3. The tire elastomeric composition according any one of the preceding claims, wherein the precipitated silica has a FWHM ranging from 100 to 250 nm.

4. The tire elastomeric composition according to any one of the preceding claims, wherein the precipitated silica has a d_{50} characterized by the following relation: $|d_{50}| > -0.81 \times |CTAB| + 263$ (IV)

5. The tire elastomeric composition according to claim 4, wherein the precipitated silica has a d_{50} between 110 nm and 240 nm, preferably between 130 and 220 nm.

6. The tire elastomeric composition according to any of the preceding claims, wherein the precipitated silica has a d_{84} characterised by the following relation: $|d_{84}| < 2.81 \times |FWHM| + 35$ (V).

7. The tire elastomeric composition according to claim 6, wherein the precipitated silica has a d_{84} comprised between 200 and 550 nm, preferably between 250 and 500 nm.

8. The tire elastomeric composition according to any one of the preceding claims, wherein the precipitated silica has a rate of fines τf of at least 92%, preferably at least of 94%, at least of 95%, at least of 97%.

9 The tire elastomeric composition according to any one of the preceding claims, wherein the content of the elastomer is more than 50 phr, more preferably at least 60 phr, more preferably at least 70 phr, even more preferably at least 80 phr, very preferably at least 90 phr.

10. The tire elastomeric composition according to any one of the preceding claims, wherein the elastomer is a dienic elastomer.

11. The tire elastomeric composition according to claim 10, wherein the elastomer is selected in the group consisting of polybutadienes, natural rubber, synthetic polyisoprenes, butadiene copolymers, isoprene copolymers and their mixtures.

12. The tire elastomeric composition according to any one of the preceding claims 10 to 11, wherein the elastomer is a functionalized diene elastomer.

13. The tire elastomeric composition according claim 12, wherein the functionalized diene elastomer comprises at least one polar function comprising at least one oxygen atom, more preferably said polar function may be selected from the group consisting of silanol, alkoxysilanes, alkoxysilanes bearing an amine group, epoxide, ethers, esters, carboxylic acids and hydroxyl.

14. The tire elastomeric composition according to any one of the preceding claims, wherein the precipitated silica constitutes at least 30% by weight, preferably at least 60%, indeed even at least 80% by weight, of the total amount of the weight of reinforcing filler.

15. The tire elastomeric composition according to any one of the preceding claims, wherein the amount of the reinforcing filler is in the range extending from 1 to 260 phr, in particular from 5 phr to 210 phr especially from 10 phr to 180 phr, for example from 20 phr to 150 phr or even from 25 phr to 140phr, even more preferably 50 to140 phr.

16. The tire elastomeric composition according to any one of the preceding claims, wherein the composition further comprising at least one plasticizing agent, the amount of said plasticizing agent being in the range extending from 10 to 150 phr, preferably from 20 to 100 phr, more preferably from 30 to 85 phr.

17. A semi-finished article for tire, comprising at least one composition according to any one of claims 1 to 16, preferably the semi-finished article being a tread.

18. A tire comprising at least one tire elastomeric composition according any one of the claims 1 to 16 or comprising at least one semi-finished article as defined in claim 17.