Abstract: Although the addition of precipitated silica confers peculiar mechanical properties to rubber compounds enabling its application in several areas, its incorporation process is extremely complex due to the difficult dispersion of silica in the elastomeric matrix, equipment wear and risk to the operators. The silica sequential precipitation process from any alkali silicate in an emulsion of latex of any origin not only enables the homogeneous distribution of silica in the elastomeric matrix, but also decreases the costs from the reduced wear of the rubber processing equipment and reduced production time, since the silica is already homogeneously incorporated into the matrix, reduction of risks due to the absence of fine particulates in the process/product environment of rubber compounds. Due to raw materials used: sulfuric acid at low concentrations and commercial purity, alkali silicate of any origin (mineral, ashes from rice husk, etc.) and the production process itself is single, i.e., two manufacturing lines are not necessary: one for production of precipitated silica and another for production of rubber, the product cost becomes competitive, enabling thus the extensive employment and production in any conventional equipment of processing of rubber compounds, besides enabling the employment of high contents of silica incorporated above 50 phr, which currently is not possible due to dispersion problems and equipment wear.
"PROCESS FOR OBTAINING COMPOUNDS THROUGH PRECIPITATION OF SILICA INTO LATEX"

FIELD OF THE INVENTION

The present invention relates to the process and additives for obtaining polymeric compounds containing functional inorganic charges (silica) and other additives through precipitation of silica in a latex composition, following the system's coagulation, filtration, washing and drying, resulting in a compound where the functional charge is uniformly distributed.

The silica particles properly precipitated "in situ" present reinforcement charges morphology and are well distributed in the polymeric matrix. These aspects are important since it is a rational process for incorporating silica in elastomers and enabling the preparation of ready compounds in a more rational manner, resulting in technical and economic benefits.

KEY-WORDS RELATED TO THE PRESENT INVENTION

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Compounds</td>
</tr>
<tr>
<td>2.</td>
<td>Silica</td>
</tr>
<tr>
<td>3.</td>
<td>Silica Masterbatch</td>
</tr>
<tr>
<td>4.</td>
<td>Rubber</td>
</tr>
<tr>
<td>5.</td>
<td>Masterbatch</td>
</tr>
<tr>
<td>6.</td>
<td>Latex</td>
</tr>
<tr>
<td>7.</td>
<td>Precipitated Silica</td>
</tr>
<tr>
<td>8.</td>
<td>Incorporated Silica</td>
</tr>
</tbody>
</table>

SUMMARY OF THE INVENTION

The present invention results on the obtainment of
amorphous precipitated silica incorporated into a polymeric matrix, named MASTERBATCH, through an innovative process from the technical and productive standpoint. This process simultaneously carries out the individual processes' stages for producing precipitated silica from an alkali silicate and the obtainment of dry rubber from synthetic or natural latex. Thereby, it is a rational process that brings economic advantages and a product (MASTERBATCH) with technical advantages due to the fact that the silica particles generated "in situ" are well distributed and more easily dispersible during the preparation process of elastomeric compounds.

The homogeneous incorporation of silica particles in the polymeric matrix may be achieved through this process developed. However, fine dispersion only happens under high shear reached in the usual rubber mixers such as Banbury, special extruders and cylinders mixer. Nonetheless, a better level of dispersion may be achieved if the process begins with MASTERBATCH instead of the individual ingredients, considering similar processing conditions.

From the operational standpoint, the mixing process via MASTERBATCH is simpler, and less harmful to operators and the equipment itself in relation, respectively, to the emission of particulate in the workplace and lesser abrasiveness of the equipment caused by MASTERBATCH compared to silica itself.
The analysis of samples obtained has evidenced the achieved benefits where the results were produced following ABNS or ASTM standardized experiment methods.

PRIOR ART

The present invention is based on the principle that elastomers may have their mechanical and chemical properties substantially improved through the reinforcement occasioned by the incorporation and dispersion of inorganic and organic particles. The substances with particles of this type are denominated reinforcement charges and/or functional charges. The level of reinforcement depends on the morphology of these particles involving the superficial area, chemical nature of the surface, size of the particles, dispersion of these particles in the polymeric matrix and also the interaction of these particles with polymeric chains and among each other.

The utilization of reinforcement charges is very important in the rubber industry, with emphasis on the carbon black (obtained from oil) and the precipitated amorphous silica (inorganic product). Carbon black is extensively used in the rubber industry, particularly in compounds for manufacturing tires and silica is subject to restrictions, particularly on processing due to equipment wear, causing higher viscosity to the compounds, which makes difficult the processing of them, in addition to the generation of static charge on the equipment.
Precipitated amorphous silica has been receiving an even higher importance in this decade, since it allows the manufacturing of elastomeric compounds with lower resistance to bearing, which allows the manufacturing of the so-called "green" tires for enabling a lower relative fuel consumption. Moreover, it provides the compounds a better adherence for the tire on wet floors, a very important property for safer driving.

To potentiate the charges function in an elastomeric compound, it is necessary that its particles are small, on the nanometric scale, properly aggregated, homogeneously distributed on the polymeric matrix and completely deagglomerated. The characteristics concerning the charges particles structured are related to the manner of obtaining their physical or chemical modification. The distribution and dispersion on the polymeric matrix are determined on compounds/composites mixture process.

The incorporation and level of dispersion of these charges on the polymer have high impact on the final performance of the composites, this process being majorly conducted "dry" in specific equipment such as "Banbury" and other mixers. This process presents inconveniences such as:

- Elevated energy consumption and wear from equipment abrasion particularly on the presence of powder or agglomerated silica;
- The material temperature is quickly elevated, forcing short mixing cycles, with insufficient particles dispersion;

- The optimal dispersion level is difficult and costly to be reached, even with the said high dispersibility types of silica;

- The dust-form charges are prone to being emanated in the environment, occasioning losses and pollution;

- The current preparation process of polymeric composites involving charges such as silica is conducted in batches, since rubber is not available in the required form (granules, etc.) in order to feed a continuous process.

The highest consumption rubbers initially are presented as latex (aqueous system) and afterwards processed for obtaining dry rubbers.

Accordingly, the obtainment of precipitated amorphous silica starts from an aqueous system and is equally processed for obtaining dry silica.

The obtainment of compounds (masterbatch) through a mixture of charges dispersed in water with latex was already explored as contained in patents BR9706372A, BR9706373A, EP1652873A1 and US2006/0205867A1. However, on the processes described there is the need to previously produce the charges dispersion, which increases costs and, also, the charges particles already formed are found with some level of
agglomeration, which hinders a fine and uniform distribution on
the mixture made (compound).

In another patent, PI 7707903, sodium silicate was
mixed with latex and the silica particles obtained via a
precipitation simultaneous with the coalescence of latex
particles - a process called co-precipitation. The major
restriction in this process is the use of elevated amounts of a
Zinc, Magnesium or Calcium salt, which remain with the product
(master) in the form of oxide. The presence of this metals
presents inconveniences, particularly Zinc, due to
environmental restrictions, which aims at reducing each time
more their presence in elastomeric compounds, besides not
presenting the same silica functionality. Moreover, according
to the process described, the incorporation of additives after
the co-precipitation is restricted.

The process defended herein, where silica
particles are generated on the latex composition itself (in
situ), adds benefits compared to the usual processes for
obtaining precipitated silica, with the specificity of
gathering processes that are currently independent, making the
product's drying and final presentation processes easier. The
compound obtained in this manner enables the simplification of
the preparation process for final composites, making them more
environmentally friendly. It also allows the formation of
silica particles already distributed in the polymeric matrix,
minimizes the formation of agglomerates without polymeric chains inserted. Through this new process, on contrary of the existing processes for obtaining precipitated silica, the physical form of silica (powder, microbead, granules, apparent density, etc.), which simplifies the process. Moreover, the final product does not present environmentally restricted substances and, after the precipitation, interest additives may be incorporated before coagulating/destabilizing the system. According to this new process, silica is found in a manner that minimizes all the aforementioned inconveniences with respect to obtaining elastomeric composites, providing the obtainment of compounds reinforced with silica in the most effective and simple manner. Furthermore, on the compound production (MASTERBATCH), the individual processes for transforming alkali silicate into precipitated silica and latex into dry rubber are rationally combined.

The composites prepared from this MASTERBATCH present similar or better characteristics than the ones obtained through conventional mixture processes used in the rubber industry.

PURPOSE OF THE INVENTION

The purpose of the present invention consists of the development of a rational and innovative process for obtaining pre-composites (MASTERBATCH), containing the elastomers, reinforcing charges and, if desired, process oil
and other additives may also be aggregated, with the following developments:

Another purpose of the present invention is the mixture of silica precursor, alkali silicate, in latex, along with the required additives and the further controlled silica precipitation in this environment. Thus, the silica particles obtained "in situ" are permeated by the other components in the system. Another purpose of the present invention is the proper formulation of latex in order for the composition to have the desired balance and allows the full separation/recovery of material on the coagulation/filtration stages.

Another purpose of the present invention is the processing conditions of this latex composition in order to obtain the mentioned MASTERBATCH, such as, for example:

- concentration of each component, pH of the system in each stage, temperature during the precipitation, form of addition, time of addition, maturation. These duly adjusted variables allow the obtainment of "in situ" silica particles with the desired morphology.

The new process allows to control, on the final stages, the desired physical form of the material, particularly the granules size, in order to make it possible to adequate them for the applications it is intended to. For example, proper granules to be used in continuous rubber composites preparation processes. The material rigidity and the additives
present leave it with a low stickiness enabling it to flow and be handled with ease.

DETAILED DESCRIPTION OF THE INVENTION

The process claimed herein is similar to the conventional process for obtaining dry elastomers from latex and also with the preparation process of precipitated silica, presenting very similar operations. This is another advantage of the present invention, since it does not imply significant additional costs compared to the individual processes.

In the process for obtaining dry elastomers after obtaining latex, the material is acidified for coagulation/destabilization, generating lumps and serum. This serum is disposed and the lumps are washed and dried.

On obtaining precipitated amorphous silica, aqueous alkali silicate is acidified under pH specific conditions, temperature, time, form of addition, etc. conditions until silica particles are obtained. The bittern is then disposed, the silica particles are washed with water and then submitted to drying.

The new process developed uses latex as source of the polymeric matrix and aqueous alkali silicate as source of functional inorganic particles. The most adequate alkali silicate for this application is sodium, with high SiO$_2$:Na$_2$O ratio, i.e., higher than 2.5, typically 3.5.

Aqueous alkali silicate may be obtained through
any source, usually sand and even ashes from rice husk; latex may be the natural one and/or synthetic, provided it is mixable with the aqueous silicate.

The other additives should be matched with the aqueous mean either through suspensions, emulsions or solutions. If necessary, surfactant agents should be incorporated in order for the system to present the desired stability, i.e., stable until the stage it should be properly destabilized.

Aqueous silicate and other desirable additives are added to latex, obtaining a latex composition, containing the elastomers, inorganic particles precursors and other desired ingredients in predefined ratios.

This latex composition is submitted to pH reduction under controlled conditions in order to cause the "in situ" formation of inorganic particles (silica) uniformly distributed in the system, enveloped by latex particles and with the proper morphology to cause the desired reinforcement in the polymer.

Then, undesired substances are removed through filtering and washing and the water itself is eliminated through drying, resulting in the desired compound (MASTERBATCH).

By the end of the process, silica is found homogeneously incorporated into the system, as well as other
predefined additives (process oil, additives acting on silica surface, etc.), besides the material being able to be presented as granules with controlled size and not agglomerated.

The process consists of the mixture of several additives to latex in a formulation involving, in dry base parts:

- Latex = 100 parts. Typically SBR latex at 20% solids content;
- Surfactants = typically 0.5 parts of sulfate type;
- pH adjusters = Alkali solution for adjusting, if necessary, latex pH, typically pH = 10;
- Emulsified oil = 5 to 100 parts, typically 10 parts;
- Aqueous silicate = 5 to 200 parts, typically 50 parts in silica equivalent. The usual silicate is sodium with silica relation: Sodium Oxide = 2 to 4:1;
- Antioxidant = typically 0.5 parts;
- Water = solids concentration adjustment;

This composition is submitted to pH reduction, under temperature controlled conditions, pH, stirring, form and time of addition and also concentration of components. Diluted sulfuric acid is the most indicated for having low cost. The pH, during precipitation, is adjusted in the range from 6 to 10, as required, and is afterwards reduced to 4 to 6, when the
composition's coagulation occurs.

The resulting composition is submitted to filtration, washing with water, drying and, if desired, leaching with water. The dried material is the product resulting from the whole process.

The tests conducted have indicated the following control values as satisfactory:

- Latex: 100 parts dry base, diluted on 20%;
- Surfactants : 0.5 parts
- pH adjusting agents: as required
- Sodium Silicate, (25% solids and Silica Ratio: Na20 = 3.5:1): equivalent to 50 parts of silica;
- Antioxidant emulsion 50%: 0.5 parts

The process consists of the following main stages:

- The ingredients are initially mixed on the above presented order under slow stirring and the pH is adjusted between 9 and 12;
- In a proper recipient (reactor), water is transferred and heated between 50 to 90°C. The latex composition without silicate may also be added and heated;
- When the temperature is reached and under vigorous stirring, the latex composition or the sodium silicate solution is added until the predefined pH is reached in the range from 7 to 10;
- The system is allowed to stand for about 10
minutes.

- The latex composition or sodium silicate and a diluted acid solution (typically sulfuric acid 10% w/w) are simultaneously added in order to maintain the predefined pH and flow rate;

- After the addition is finished, the system is matured for about 10 minutes, and acid is added until a pH close to 5 is reached.

- If necessary, coagulation ancillaries are added to this new latex composition;

- The slurry is filtered, washed with water and crammed. The resulting conformed mass is dried in a greenhouse or in other static convenient manner, overall dynamic, preventing high temperatures. During the drying, the material is moved to facilitate the drying and also allows the control of granules size.

  When the material is nearly dry (about 10% humidity) it may be laminated to make drying easier and giving it an alternative final shape;

The dry composition (master) is analyzed as such and also as an elastomeric compound prepared in conventional mixers, adding activators (Zinc Oxide and Stearic Acid), the vulcanizing agents (sulfur and vulcanizing accelerators), and surface modifiers such as polyethylene glycol, Silanes, etc. may be added.
The composites below were prepared in cylinders mixer, following the usual procedure, using formulations in table 1, quantities in phr:

**Table 1**: Formulations of the tested composites

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>REF</th>
<th>Example 1</th>
<th>Example 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBR 1502</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Commercial Silica¹</td>
<td>30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Master Obtained</td>
<td>-</td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>PEG 4000²</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>TESPT³</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Estearic Acid</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>TBBS⁴</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.75</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>140.75</strong></td>
<td><strong>140.75</strong></td>
<td><strong>140.75</strong></td>
</tr>
</tbody>
</table>

1 - Commercial product, with BET = 175

2 - Polyethylene Glycol with PM = 4000

3 - bis (triethoxysilylpropyl) tetrasulphide

4 - N-tert-butyl-2-benzothiazole sulfenamide

**Table 2**: Properties of the tested composites

<table>
<thead>
<tr>
<th>Item</th>
<th>KEF</th>
<th>Example 1</th>
<th>Example 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minimum torque, dN.m¹</td>
<td>8.20</td>
<td>10.80</td>
<td>6.70</td>
</tr>
<tr>
<td>Maximum torque, dN.m¹</td>
<td>42.00</td>
<td>39.40</td>
<td>27.60</td>
</tr>
</tbody>
</table>
Scorch Time, minisec
Optimal healing time, minisec
Hardness, Shore A
Module 300%, MPa
Rupture Tension, MPa
Elongation at Break, %

<table>
<thead>
<tr>
<th></th>
<th>5:30</th>
<th>6:33</th>
<th>9:50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scorch Time, minisec</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Optimal healing time,</td>
<td>15:50</td>
<td>26:33</td>
<td>29:00</td>
</tr>
<tr>
<td>Hardness, Shore A</td>
<td>63</td>
<td>62</td>
<td>58</td>
</tr>
<tr>
<td>Module 300%, MPa</td>
<td>6.3</td>
<td>6.5</td>
<td>3.4</td>
</tr>
<tr>
<td>Rupture Tension, MPa</td>
<td>14.8</td>
<td>17.0</td>
<td>17.2</td>
</tr>
<tr>
<td>Elongation at Break, %</td>
<td>480</td>
<td>440</td>
<td>640</td>
</tr>
</tbody>
</table>

1 - Rheometer curve obtained in MDR type equipment, at 150°C, 35min.

The results presented obtained in Table 2 allow us to verify the following, always comparing to the reference composite (REF). It is important to consider that MATERBATCH in example 1 was obtained on a "pilot" scale and in example 2 in "laboratorial" scale, as the components quantities for each component indicate:

- The simplicity for preparing the composites was very evident. The master immediately grouped in the mixer roll and the mixture was finalized in instants;
- Concerning the molding and vulcanization, all composites had similar behavior, except the longest vulcanization times, but these may be adjusted through MASTER productive process or through formulation;
- The hardness obtained is within the expected and consistent with what is expected from a reinforcing charge;
- The Rupture Tension, which is a good parameter
for assessing the reinforcement reached, is superior, indicating that the silica particles obtained "in situ" present proper morphology and are well dispersed in the polymeric matrix. The Rupture Tension of SBR 1502 composite without charge - called pure gum, is between 2 and 4 Mpa; which means, reinforcement really occurred.

Example 1:

In a recipient, the following was mixed: 20 kg of SBR latex (Styrene Butadiene Rubber) with 20% dry rubber content; 50 g of anionic surfactant; 50 g of non-anionic surfactant; 50 g of Triethanolamine (TEA); NaOH at 10% for adjusting the pH at 10 and 6 kg of sodium silicate at 20% silica content and 4:1 SiO2:Na2O relation.

In a reactor made from stainless steel, jacketed, with controllable agitation of up to 1700rpm attached and naval-type rod, 50 liters of water were transferred. After reaching a 70°C temperature, 1 kg of the latex composition was added. Up next, sulfuric acid at 10% was added until the pH was reduced to 9.0, under vigorous agitation. After 10 minutes, under a 80°C temperature, the simultaneous addition of the latex composition and the solution of sulfuric acid at 10% was commenced, keeping the pH at 8.5 and under vigorous agitation. The flow rate was adjusted in a manner that the addition time was 1 hour. After 10 minutes from finishing the simultaneous addition, reducing the temperature to 70°C, the solution was
acidified to pH 6 with sulfuric acid. Then, a solution with sulfuric acid and coagulation ancillary was added until pH 4 was obtained. The system was destabilized.

The resulting lumps were separated from the serum through filtration and washed with water afterwards. Then, drying at 90°C was conducted until constant weight was obtained.

**Example 2:**

In a glass recipient, the following was mixed: 300 g of SBR latex (Styrene Butadiene Rubber) with 25% dry rubber content; 1 g of anionic surfactant; 1 g of non-ionic surfactant; 2 g of Triethanolamine (TEA); 2 g NaOH at 10%; 120 g of sodium silicate at 20% silica content and 4:1 Si02:Na20 relation; and 100 g of water. In an addition funnel, the latex composition was placed. In another dripped, a sulfuric acid solution at 5% was placed. In another glass recipient, 400 g of water was placed and heated in bain-marie at 80°C. A total of 10 g from the latex composition was transferred to this recipient, then the acid solution was dripped until a pH 9 was reached, under vigorous agitation (900 rpm, naval-type rod). Afterwards, the simultaneous dripping commenced, under agitation, in order to maintain the pH close to 9.0. At the end of 30 minutes of addition, the temperature was reduced to 70°C and acid was added until pH 6 was reached. Then, a solution of sulfuric acid and coagulation ancillary was added until pH 4.
was obtained. The system coagulated, was filtered, the lumps were dried and the resulting mass was crammed. Then it was dried in a greenhouse at 90°C until constant weight was obtained.

**Example 3:**

In a recipient, the following was mixed: 22.5 kg of SBR latex (Styrene Butadiene Rubber) with 20% dry rubber content; 50 g of anionic surfactant; 50 g of non-ionic surfactant; 50 g of Triethanolamine (TEA); NaOH at 10% to adjust the pH at 10 and 15.5 kg of sodium silicate at 20% silica content and 4:1 SiO2:Na20 relation.

On the same reactor from Example 1, 50 liters of water were transferred. After reaching an 80°C temperature, 2.5 kg of the latex composition were added. Then, sulfuric acid at 10% was added until reducing the pH to 9.0 under vigorous agitation. After 10 minutes, at an 85°C temperature, the simultaneous addition of the latex composition and the 10% sulfuric acid solution was added, maintaining the pH at 9.2 and under vigorous agitation. The flow rate was adjusted in order for the addition time to be 1 hour. Soon after, 200 g of TESPT was added, in the form of emulsion. After 30 minutes, the temperature was reduced to 70°C and the contents were acidified with the sulfuric acid solution until pH 6. Then, a solution with sulfuric acid and coagulation ancillary was added until pH 4 was obtained. The system completely destabilized.
The resulting lumps were separated from the clear serum through filtration and washed afterwards with water. Then, the drying at 90°C was conducted until constant weight was achieved. Example 4: in a recipient, the following was mixed: 23 kg of SBR latex (Styrene Butadiene Rubber) with 20% dry rubber content; 50 g of Triethanolamine (TEA); NaOH at 10% to adjust the pH at 10 and 16 kg of sodium silicate at 20% silica content and 4:1 SiO2:Na2O relation.

On the same reactor from Example 1, 50 liters of water were transferred. After reaching an 80°C temperature, 3 kg of the latex composition were added. Then, sulfuric acid at 10% was added until the pH was reduced to 9.0, under vigorous agitation. After 10 minutes, under an 85°C temperature, the simultaneous addition of the latex composition and the solution of sulfuric acid at 10% commenced, maintaining the pH at 9.2 under vigorous agitation.

The flow rate was adjusted in order for the addition time to be 1 hour and 15 minutes. Soon after, 250 g of TESPT was added, in the form of emulsion. After 60 minutes, the temperature was reduced to 70°C and the contents were acidified with the sulfuric acid solution until pH 6 was obtained. Then, a solution with sulfuric acid and coagulation ancillary was added until pH 4 was obtained. The system completely destabilized.

The resulting lumps were separated from the clear
serum through filtration and washed afterwards with water.

Next, the drying at 90°C was conducted until constant weight was obtained.

**Table 3**: Formulations of the composites, quantities in phr

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Example 3</th>
<th>Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Master Obtained</td>
<td>176.0</td>
<td>176.0</td>
</tr>
<tr>
<td>PEG 4000¹</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>6PPD²</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>TMQ³</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Estearic Acid</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>TBBS⁴</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Sulfur</td>
<td>1.75</td>
<td>1.75</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td><strong>188.25</strong></td>
<td><strong>188.25</strong></td>
</tr>
</tbody>
</table>

1 - PM Polyethylene Glycol = 4000

2 - N-(1, 3-dimethylbutyl) -N-phenyl-p-phenylenediamine

3 - 2,2,4-trimethyl-1, 2- dihydroquinoline polymerized

4 - N-tert-butyl-2-benzothiazole sulfenamide

The composites were firstly processed in a laboratory mixer type Banbury, adding the Master and the protection agents (6 PPD and TMQ): tangential rotor, 60rpm, 4 minutes, and discharge at approximately 145°C. Then, the
mixture was finalized in an open cylinders mixer.

Table 4: Composites properties

<table>
<thead>
<tr>
<th>Item</th>
<th>Example 3</th>
<th>Example 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visc. Mooney, CML 1 + 4 (100°C)</td>
<td>99</td>
<td>138</td>
</tr>
<tr>
<td>Minimum torque, dN.m(^1)</td>
<td>3.7</td>
<td>5.4</td>
</tr>
<tr>
<td>Maximum torque, dN.m(^1)</td>
<td>27.5</td>
<td>35.4</td>
</tr>
<tr>
<td>Scorch time, min:sec(^1)</td>
<td>3.4</td>
<td>2.7</td>
</tr>
<tr>
<td>Optimal healing time, min:sec(^1)</td>
<td>11.9</td>
<td>12.3</td>
</tr>
<tr>
<td>Hardness, Shore A</td>
<td>70</td>
<td>75</td>
</tr>
<tr>
<td>Module at 300%, MPa</td>
<td>10.8</td>
<td>9</td>
</tr>
<tr>
<td>Rupture Tension, MPa</td>
<td>42.4</td>
<td>42.1</td>
</tr>
<tr>
<td>Elongation at Break, %</td>
<td>650</td>
<td>630</td>
</tr>
<tr>
<td>Resist. To Ripping, N/mm</td>
<td>70.2</td>
<td>86.0</td>
</tr>
<tr>
<td>Hydrostatic Density, g/cm(^3)</td>
<td>1.214</td>
<td>1.203</td>
</tr>
<tr>
<td>Relative volume loss, mm(^3)</td>
<td>114</td>
<td>118</td>
</tr>
</tbody>
</table>

1 - Rheometer curve obtained in equipment type RPA, at 160°C, 30 min, 100 com.

It is important to emphasize that, upon observing the results on Table 4, the Rupture Tension and Resistance to Ripping values are very high, approximately 40% higher than the current prior art, without prejudice to the other characteristics of these composites.

DMA EXEMPLE 3

Dimensions: 1.95 x 9.35 x 10.05 mm
Equipment: DMA 2980 TA Instruments

Method: Heating 2°C/min until 70°C - 15 μm Amplitude - 2 Hz Frequency

Table 5 - Delta Tangent Values Comparison at 60°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Delta Tangent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference</td>
<td>0.152</td>
</tr>
<tr>
<td>Example 3</td>
<td>0.134</td>
</tr>
<tr>
<td>Example 4</td>
<td>0.150</td>
</tr>
</tbody>
</table>

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2 - Reducing zinc oxide in rubber industry use through the
development of mixed metal oxide nanoparticles Manuel Guzman,
Niiria Agullo, Salvador Borros Grup d'Enginyeria de Materials
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CLAIMS

1. A process for preparing rubber compounds with silica incorporated through sequential silica precipitation from a alkali silicate and this latex composition, wherein the silica precipitation firstly occurs with controlled morphologic properties and following coagulation of the latex composition, and the silica is homogeneously distributed into rubber coagulates/lumps.

2. A process according to claim 1, wherein the alkali silicate can be directly added to the reaction mean or can be preferentially mixed to the latex.

3. A process according to claim 1, wherein both the raw materials latex and alkali silicate are simultaneously added to the reactor;

4. A process according to claim 1, wherein the sodium silicate can be from mineral origin, ashes from rice husk and others;

5. A process according to claim 1, wherein low cost acids are used in the precipitation, preferentially a commercial sulfuric acid at 98% and the lowest cost-benefit ratio, i.e. less than R$0.90/kg;

6. A process according to claim 1, wherein the silica precipitation pH from alkali silicate is between 7 and 9;

7. A process according to claim 6, wherein the
alkali silicate concentration enables the incorporation of any silica contents in the rubber matrix at an interval from 5 to 200phr;

8. A process according to claim 1, wherein any latex concentration can be used for the manufacturing of compounds, considering that it can be diluted within the range from 1 to 70%;

9. A process according to claim 1, wherein the stirring high process conditions are from 700 to 1750 rpm;

10. A process according to claim 1, wherein the reaction temperature is between 60 and 90°C;

11. The product according to claim 1 to 10, wherein Masterbatch is originated from this process with several silica quantities incorporated and different types of latex;

12. The product according to claim 11, wherein it can be used in the manufacturing of rubbers of any nature.