Abstract:
A composition including an aluminosilicate and a flux, where the aluminosilicate and the flux are calcined to form calcined granules is disclosed. A method including adding a flux to an aluminosilicate to form a mixture and calcining the mixture to form calcined granules is also disclosed. The aluminosilicate may include kaolin and/or chamotte. The flux may include a salt, sodium silicate, or potassium feldspar. The composition may be calcined at a temperature less than about 1300°C. The calcined granules may be coated with a hydrophobic coating. The hydrophobic coating may include a silane or siloxane. The calcined granules may have a hardness greater than 4.5 Mohs.
ULTRAWHITE ROOFING GRANULES

CLAIM FOR PRIORITY

[0001] This PCT International Application claims the benefit of priority of U.S. Provisional Application No. 61/929,721, filed January 21, 2014, the subject matter of which is incorporation herein by reference in its entirety.

FIELD OF DISCLOSURE

[0002] Disclosed herein are compositions for ultrawhite granules, such as for use in roofing compositions.

BACKGROUND OF THE DISCLOSURE

[0003] A "cool roof" is one that reflects the sun's heat and emits absorbed radiation back into the atmosphere. When a roof stays cooler, it may reduce the amount of heat transferred to the building below, keeping the building cooler and helping to maintain a more constant temperature. Some states and large cities are considering or beginning to require "cool roof technologies to reduce energy costs and/or the "heat island" effect, in which cities are several degrees warmer than the surrounding land.

[0004] Roofing materials, such as bitumen, can be used in roof surfaces, such as shingles. Granules may be added to a roofing material to provide coloring and abrasion resistance. Calcined kaolin granules may have some desirable properties that may aid the roofing material in acting as a "cool roof." However, calcining kaolin granules requires high firing temperatures, around 1500°C, to achieve desirable "cool roof" properties, such as high hardness. Such high firing temperatures make formation of the granules difficult and expensive, and may require use of specialized high-
temperature equipment. Such high firing temperatures may also adversely affect certain desirable properties, such as lowering the whiteness value.

[0005] Thus, it would be desirable to provide lower-cost granules with equivalent or improved "cool roof" properties. It may also be desirable to create an aluminosilicate-based roofing granule, such as, for example, a kaolin-based roofing granule, that is capable of reflecting and emitting the energy of the sun. It may be further desirable to provide a granule that reduces the amount of heat transferred to a roof and building, resulting in temperature regulation and reduction of energy costs.

SUMMARY

[0006] A composition comprises an aluminosilicate and a flux, wherein the aluminosilicate and the flux are calcined to form calcined granules.

[0007] A method comprises adding a flux to an aluminosilicate to create a mixture, and calcining the mixture to create calcined granules.

[0008] A method comprises adding a flux to an aluminosilicate to create a mixture, calcining the mixture to create calcined granules, and adding the calcined granules to a roofing material.

[0009] The aluminosilicate may include at least one of kaolin and chamotte.

[0010] The calcined granules may be coated with a hydrophobic coating. The hydrophobic coating may include, for example, a silane or siloxane coating. Siloxanes may include unfunctionalized siloxanes (e.g., silicones). The calcined granules may not be coated.

[0011] The roofing material may include bitumen.
DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0012] A composition may comprise an aluminosilicate and a flux, wherein the aluminosilicate and the flux are calcined to form calcined granules. The aluminosilicate may be a naturally occurring aluminosilicate, such as, for example, kaolin. The kaolin may comprise hydrous kaolin. The aluminosilicate may comprise chamotte.

[0013] Hereafter, certain embodiments may tend to be discussed in terms of kaolin. The invention should not be construed as being limited to such embodiments, as it will be understood that the kaolin may be replaced, either in whole or in part, with other aluminosilicate materials.

[0014] Although certain embodiments may tend to discuss the flux in terms of sodium silicate or potassium feldspar, it will be understood that the invention should not be construed as being limited to such embodiments. Similarly, although certain embodiments may tend to discuss the hydrophobic coating in terms of siloxane, it will also be understood that the invention should not be construed as being limited to such embodiments.

[0015] The calcined granules may have a platy shape, with a high aspect ratio. Other shapes may increase the surface coverage of the granules when adhered to a roofing material, including, for example, irregular shapes that improve the packing density of the calcined granules.

[0016] Prior to calcining, the aluminosilicate, such as kaolin and/or chamotte, and the flux may be mixed to form a mixture. The mixture may be extruded to form, for example, a green body. The green body may be calcined in a firing vessel, such as, for example, a furnace or kiln. The calcined body may then be crushed, milled, or ground to form the granules. The crushing, milling, or grinding may be used to obtain a desired
granule size distribution. Crushing may be performed, for example, by a jaw crusher. Milling may be performed, for example, by a ball mill, hammer mill, or roller mill. Grinding may comprise wet or dry grinding. The crushing, milling, or grinding may be performed individually or in combination to obtain a desired granule size distribution.

[0017] The amount of flux may be the weight percent (wt%) measured as the weight of the flux material over the total weight of the granule material prior to calcining.

[0018] In some embodiments, a solubilizing agent may be added to the flux to promote mixing of the flux with the kaolin. The solubilizing agent may be added to the flux prior to or during mixing of the flux and the kaolin. The solubilizing agent may include, for example, water or organic solvents (e.g., alcohols).

[0019] According to some embodiments, the amount of flux relative to the total weight of the granule material may comprise at least 5wt% flux, for example, at least 7.5wt% flux, at least 10.5wt% flux, or at least 12.5wt% flux. In some embodiments, the amount of flux may comprise less than 15wt% flux. In some embodiments, the amount of flux relative to the total weight of the granule material may comprise between 5wt% and 15wt% flux, for example, between 5wt% and 12.5wt% flux, between 7.5wt% and 12.5wt% flux, or between 10wt% and 12.5wt% flux.

[0020] In some embodiments, the flux comprises a salt. The salt may include a Group I salt, such as, for example, sodium silicate. The amount of flux relative to the total weight of the granule material may comprise less than 15wt% sodium silicate. The amount of flux may comprise between 5wt% and 15wt% sodium silicate, for example, between 5wt% and 12.5wt% sodium silicate, between 7.5wt% and 15wt% sodium silicate, between 7.5wt% and 12.5wt% sodium silicate, between 7.5wt% and 10wt%
sodium silicate, or between 10wt% and 12.5wt% sodium silicate. In some embodiments, the salt may include, for example, a Group II or Group III salt.

[0021] In some embodiments, the flux may comprise potassium feldspar. The amount of flux relative to the total weight of the granule material may comprise less than 25wt% potassium feldspar, for example, less than 20wt% potassium feldspar. In some embodiments, the amount of flux may comprise between 20wt% and 25wt% potassium feldspar.

[0022] In some embodiments, the calcined granule may be coated with a hydrophobic coating. In some embodiments, the hydrophobic coating may include at least one silane. In some embodiments, the hydrophobic coating may include at least one siloxane. Siloxanes may include unfunctionalized siloxanes (e.g., silicones). The silane may contain other elements, for example, nitrogen or fluorine (e.g., fluorinated silane). In some embodiments, the calcined granule may not be coated.

[0023] In general, silanes and other monomeric silicon compounds may have the ability to bond to inorganic materials. In some embodiments, the silane may include at least one ionic silane. Exemplary ionic silanes include, but are not limited to, 3-(trimethoxysilyl)propyl-ethylenediamine triacetic acid trisodium salt and 3-(trihydroxysilyl)propylmethylposphonate salt. In another embodiment, the silane may include at least one non-ionic silane.

[0024] In further embodiments, the silane may include moieties, including, but not limited to, alkoxy, halogen, hydroxy, aryloxy, amino, amide, methacrylate, mercapto, carbonyl, urethane, pyrrole, carboxy, cyano, aminoacyl, acylamino, alkyl ester, aryl ester, substituted or unsubstituted alkyl, alkenyl, alkaryl, alkycycloalkyl, aryl, cycloalkyl,
cycloalkenyl, heteroaryl, heterocyclic, cycloalkaryl, cycloalkenylaryl, alkycycloalkaryl, alkycycloalkenyl, arylalkaryl, hydrogen, alkyl, alkenyl, alkaryl, alkycycloalkyl, aryl, cycloalkyl, cycloalkenyl, heteroaryl, heterocyclic, cycloalkaryl, cycloalkenylaryl, alkycycloalkaryl, alkycycloalkenylaryl, arylalkaryl, alkoxy, halogen, hydroxy, aryloxy, amino, amide, methacrylate, mercapto, carbonyl, urethane, pyrrole, alkyl ester, aryl ester, carboxy, sulphonate, cyano, aminoacyl, acylamino, epoxy, phosphonate, isothiouronium, thiouronium, alkylamino, quaternary ammonium, trialkylammonium, alkyl epoxy, alkyl urea, alkyl imidazole, or alkylisothiouronium.

[0025] In general, siloxanes are any of a class of organic or inorganic chemical compounds comprising silicon, oxygen, and often carbon and hydrogen.

[0026] Exemplary silanes and siloxanes include, but are not limited to, dimethylsiloxane, methylphenylsiloxane, methylhydrogen siloxane, methylhydrogen polysiloxane, methyltrimethoxysilane, octamethylcyclotetrasiloxane, hexamethyldisiloxane, octyldiethoxysilane, diphenylsiloxane, unfunctionalized siloxanes (e.g., silicones), and copolymers or blends of copolymers of any combination of monophenylsiloxane units, diphenylsiloxane units, phenylmethylsiloxane units, dimethylsiloxane units, monomethylsiloxane units, vinylsiloxane units, phenylvinylsiloxane units, methylvinylsiloxane units, ethylsiloxane units, phenylethylsiloxane units, ethylmethylsiloxane units, ethylvinylsiloxane units, octyldiethoxysilane units, or diethylsiloxane units.

[0027] In some embodiments, the amount of hydrophobic coating, for example, siloxane, relative to the weight of the fired granule may comprise at least 0.5wt% siloxane. The amount of siloxane relative to the weight of the fired granule comprises
less than 1 wt% siloxane, for example, less than 0.9 wt% siloxane, less than 0.8 wt% siloxane, less than 0.75 wt% siloxane, less than 0.7 wt% siloxane, or less than 0.65 wt% siloxane. According to some embodiments the amount of siloxane relative to the weight of the fired granule may comprise between 0.5 wt% and 0.65 wt% siloxane. Although the examples may be discussed in terms of siloxane, it will be understood that the invention should not be construed as being limited to such embodiments and that similar weights of hydrophobic coating, for example, a silane, may be used.

[0028] In some embodiments, the amount of hydrophobic coating relative to the weight of the fired granule may comprise at least 0.5 wt% hydrophobic coating. The amount of hydrophobic coating relative to the weight of the fired granule comprises less than 1 wt% hydrophobic coating, for example, less than 0.9 wt% hydrophobic coating, less than 0.8 wt% hydrophobic coating, less than 0.75 wt% hydrophobic coating, less than 0.7 wt% hydrophobic coating, or less than 0.65 wt% hydrophobic coating. According to some embodiments the amount of hydrophobic coating relative to the weight of the fired granule may comprise between 0.5 wt% and 0.65 wt% hydrophobic coating.

[0029] In some embodiments, the calcined granules have a hardness greater than 4.5 Mohs, for example, greater than 5.0, greater than 5.5, greater than 6.0, greater than 6.5, greater than 7.0, or greater than 7.5 Mohs. The Mohs hardness may be measured according to the test method SC-T-7.

[0030] In some embodiments, the calcined granules have a whiteness greater than 90, for example, greater than 91, greater than 92, greater than 93, or greater than 94. The whiteness may be the Hunter whiteness, L*. In some embodiments, the calcined granules have a yellowness less than 10, for example, less than 9, less than 8,
less than 7, less than 6, or less than 5. The yellowness may be a Hunter yellowness, b*. Whiteness and yellowness may be measured, for example, according to the ARMA test method "Roofing Granules Color Measurement Procedure.".

[0031] According to some embodiments, the calcining is performed at a temperature less than or equal to about 1300°C, for example, less than or equal to about 1250°C, or less than or equal to about 1200°C. In other embodiments, the calcining is performed at a temperature less than or equal to about 1500°C, for example, less than or equal to about 1400°C. According to some embodiments, the calcining is performed at a temperature of at least about 600°C, such as, for example, at least about 800°C, at least about 1000°C, at least about 1200°C, or at least about 1400°C. The calcining may be performed in an appropriate firing vessel, such as a furnace or kiln.

[0032] The term "calcining," as used in this disclosure refers to heating a material to a temperature below the melting point in order to bring about a thermal decomposition, phase transition, or removal of volatile components. For a given material, one of ordinary skill in the art would understand how to determine a minimum calcining temperature.

[0033] In some embodiments, the calcined granules have a solar reflectance of at least 0.80, for example, at least 0.81, at least 0.82, at least 0.83, at least 0.85, at least 0.85, or at least 0.86. As used in this disclosure, the term "solar reflectance" or "solar reflectivity" represents the quantity measured by a solar spectrum reflectometer, for example, as determined by ASTM standard C1549.
In some embodiments, less than 0.1% of the calcined granules have a granule size greater than 2.36mm. Between 4% and 10% of the calcined granules may have a granule size less than 2.36mm and greater than 1.7mm, between 30% and 50% of the calcined granules may have a granule size less than 1.7mm and greater than 1.18mm, between 10% and 30% of the calcined granules may have a granule size less than 850µm and greater than 600µm, between 1% and 10% of the calcined granules may have a granule size less than 600µm and greater than 425µm, or less than 2% of the calcined granules may have a granule size less than 425µm. According to some embodiments, the distribution of calcined granules is shown in Table 1.

<table>
<thead>
<tr>
<th>Granule size</th>
<th>% of Calcined Granules</th>
</tr>
</thead>
<tbody>
<tr>
<td>&gt;2.36mm (8 mesh)</td>
<td>&lt;0.1%</td>
</tr>
<tr>
<td>1.70mm - 2.36mm (12 mesh)</td>
<td>4-10%</td>
</tr>
<tr>
<td>1.18mm - 1.70mm (16 mesh)</td>
<td>30-50%</td>
</tr>
<tr>
<td>850µm - 1.18mm (20 mesh)</td>
<td>20-40%</td>
</tr>
<tr>
<td>600µm - 850µm (30 mesh)</td>
<td>10-30%</td>
</tr>
<tr>
<td>425µm - 600µm (40 mesh)</td>
<td>1-10%</td>
</tr>
<tr>
<td>&lt;425µm (-40 mesh)</td>
<td>&lt;2%</td>
</tr>
</tbody>
</table>

**TABLE 1**

According to some embodiments, a method comprises adding a flux to an aluminosilicate to create a mixture, and calcining the mixture to form calcined granules. The aluminosilicate may be a naturally-occurring aluminosilicate, such as, for example, kaolin and/or chamotte.

Prior to calcining, the mixture may be extruded to form, for example, a green body. The green body may be calcined in, for example, a furnace or kiln. The calcined body may then be crushed, milled, or ground to form the granules. The crushing, milling, or grinding may be used to obtain a desired granule size distribution.
Crushing may be performed, for example, by a jaw crusher. Milling may be performed, for example, by a ball mill, hammer mill, or roller mill. Grinding may comprise wet or dry grinding. The crushing, milling, or grinding may be performed individually or in combination to obtain a desired granule size distribution.

[0037] In some embodiments, a solubilizing agent may be added to the flux to promote mixing of the flux with the aluminosilicate, such as kaolin and/or chamotte. The solubilizing agent may be added to the flux prior to or during mixing of the flux and the aluminosilicate. The solubilizing agent may include, for example, water or organic solvents (e.g., alcohols).

[0038] According to some embodiments, the amount of flux relative to the total weight of the granule material may comprise at least 5wt% flux, for example, at least 7.5wt% flux, at least 10.5wt% flux, or at least 12.5wt% flux. In some embodiments, the amount of flux may comprise less than 15wt% flux. In some embodiments, the amount of flux may comprise between 5wt% and 15wt% flux, for example, between 5wt% and 12.5wt% flux, between 7.5wt% and 12.5wt% flux, or between 10wt% and 12.5wt% flux.

[0039] In some embodiments, the flux comprises a salt. The salt may include a Group I salt, for example, sodium silicate. The amount of flux relative to the total weight of the granule material may comprise less than 15wt% sodium silicate. The amount of flux may comprise between 5wt% and 15wt% sodium silicate, for example, between 5wt% and 12.5wt% sodium silicate, between 7.5wt% and 15wt% sodium silicate, between 7.5wt% and 12.5wt% sodium silicate, between 7.5wt% and 10wt% sodium silicate, or between 10wt% and 12.5wt% sodium silicate. In some embodiments, the salt may include, for example, a Group II or Group III salt.
In some embodiments, the flux may comprise potassium feldspar. The amount of flux relative to the total weight of the granule material may comprise less than 25wt% potassium feldspar, for example, less than 20wt% potassium feldspar. In some embodiments, the amount of flux may comprise between 20wt% and 25wt% potassium feldspar.

In some embodiments, the calcined granule may be coated with a hydrophobic coating. In some embodiments, the hydrophobic coating may include at least one silane. In some embodiments, the hydrophobic coating may include at least one siloxane. The silane may contain other elements, for example, nitrogen or fluorine (e.g., fluorinated silane).

In general, silanes and other monomeric silicon compounds may have the ability to bond to inorganic materials. In some embodiments, silane may include at least one ionic silane. Exemplary ionic silanes include, but are not limited to, 3-(trimethoxysilyl)propyl-ethylenediamine triacetic acid trisodium salt and 3-(trihydroxysilyl)propylmethylphosphonate salt. In another embodiment, the silane includes at least one non-ionic silane.

In further embodiments, the silane may include moieties, including, but not limited to, alkoxyl halogen, hydroxy, aryloxy, amino, amide, methacrylate, mercapto, carbonyl, urethane, pyrrole, carboxy, cyano, aminoacyl, acylamino, alkyl ester, aryl ester, substituted or unsubstituted alkyl, alkenyl, alkaryl, alkycycloalkyl, aryl, cycloalkyl, cycloalkenyl, heteroaryl, heterocyclic, cycloalkaryl, cycloalkenylaryl, alkycycloalkaryl, alkycycloalkenylaryl, arylalkaryl, hydrogen, alkyl, alkenyl, alkaryl, alkycycloalkyl, aryl, cycloalkyl, cycloalkenyl, heteroaryl, heterocyclic, cycloalkaryl, cycloalkenylaryl,
alkycloalkaryl, alkcycloalkenyaryl, aryialkaryl, alkoxy, halogen, hydroxy, aryloxy, amino, amide, methacrylate, mercapto, carbonyl, urethane, pyrrole, alkyl ester, aryl ester, carboxy, sulphonate, cyano, aminoacyl, acylamino, epoxy, phosphonate, isothiouronium, thiouronium, alkylamino, quaternary ammonium, trialkylammonium, alkyl epoxy, alkyl urea, alkyl imidazole, or alkylisothiouronium.

[0044] In general, siloxanes are any of a class of organic or inorganic chemical compounds comprising silicon, oxygen, and often carbon and hydrogen.

[0045] Exemplary silanes and siloxanes include, but are not limited to, dimethylsiloxane, methylphenylsiloxane, methylhydrogen siloxane, methylhydrogen polysiloxane, methyltrimethoxysilane, octamethylcyclotetrasiloxane, hexamethyldisiloxane, octyltriethoxysilane, diphenylsiloxane, unfunctionalized siloxanes (e.g., silicones), and copolymers or blends of copolymers of any combination of monophenylsiloxane units, diphenylsiloxane units, phenylmethylsiloxane units, dimethylsiloxane units, monomethylsiloxane units, vinylsiloxane units, phenylvinylsiloxane units, methylvinylsiloxane units, ethylsiloxane units, phenylethylsiloxane units, ethylmethylsiloxane units, ethylvinylsiloxane units, octyltriethoxysilane units, or diethylsiloxane units.

[0046] In some embodiments, the amount of hydrophobic coating, for example, siloxane, relative to the weight of the fired granule may comprise at least 0.5wt% siloxane. The amount of siloxane relative to the weight of the fired granule comprises less than 1wt% siloxane, for example, less than 0.9wt% siloxane, less than 0.8wt% siloxane, less than 0.75wt% siloxane, less than 0.7wt% siloxane, or less than 0.65wt% siloxane. According to some embodiments the amount of siloxane relative to the weight
of the fired granule may comprise between 0.5wt% and 0.65wt% siloxane. Although the examples may be discussed in terms of siloxane, it will be understood that the invention should not be construed as being limited to such embodiments and that similar weights of hydrophobic coating, for example, a silane, may be used.

[0047] In some embodiments, the amount of hydrophobic coating relative to the weight of the fired granule may comprise at least 0.5wt% hydrophobic coating. The amount of hydrophobic coating relative to the weight of the fired granule comprises less than 1wt% hydrophobic coating, for example, less than 0.9wt% hydrophobic coating, less than 0.8wt% hydrophobic coating, less than 0.75wt% hydrophobic coating, less than 0.7wt% hydrophobic coating, or less than 0.65wt% hydrophobic coating. According to some embodiments the amount of hydrophobic coating relative to the weight of the fired granule may comprise between 0.5wt% and 0.65wt% hydrophobic coating.

[0048] In some embodiments, the calcined granules have a hardness greater than 4.5 Mohs, for example, greater than 5.0, greater than 5.5, greater than 6.0, greater than 6.5, greater than 7.0, or greater than 7.5 Mohs.

[0049] In some embodiments, the calcined granules have a whiteness greater than 90, for example, greater than 91, greater than 92, greater than 93, or greater than 94. In some embodiments, the calcined granules have a yellowness less than 10, for example, less than 9, less than 8, less than 7, less than 6, or less than 5.

[0050] According to some embodiments, the calcining is performed at a temperature less than or equal to about 1300°C, for example, less than or equal to about 1250°C, or less than or equal to about 1200°C. In other embodiments, the calcining is performed at a temperature less than or equal to about 1500°C, for
example, less than or equal to about 1400°C. According to some embodiments, the
calcining is performed at a temperature of at least about 600°C, such as, for example, at
least about 800°C, at least about 1000°C, at least about 1200°C, or at least about
1400°C. The calcining may be performed in an appropriate firing vessel, such as a
furnace or kiln.

[0051] In some embodiments, the calcined granules have a solar reflectance of
at least 0.80, for example, at least 0.81, at least 0.82, at least 0.83, at least 0.85, at
least 0.85, or at least 0.86.

[0052] In some embodiments, less than 0.1% of the calcined granules have a
granule size greater than 2.36mm. Between 4% and 10% of the calcined granules may
have a granule size less than 2.36mm and greater than 1.7mm, between 30% and 50%
of the calcined granules may have a granule size less than 1.7mm and greater than
1.18, between 10% and 30% of the calcined granules may have a granule size less
than 850μιη and greater than 600μιη , between 1% and 10% of the calcined granules
may have a granule size less than 600μιη and greater than 425μιη , or less than 2% of
the calcined granules may have a granule size less than 425μιη . An exemplary
distribution of calcined granule sizes is shown in Table 1 above.

[0053] According to some embodiments, the calcined granules may be added
to a roofing material, such as, for example, bitumen.

[0054] According to certain embodiments, by mixing in a flux (e.g., sodium
silicate) with the kaolin prior to calcination, less flux may be used as compared to using
the flux as a binder for previously calcined kaolin. In some embodiments, the mixing of
a flux with the kaolin allows the resulting composition to be fired at a lower temperature
to achieve an acceptable level of whiteness and hardness. The ability to prepare high-hardness, high-whiteness calcined-kaolin granules at relatively lower temperatures may reduce the cost of preparing the granules. Calcining at a relatively lower temperature may also permit less expensive or more common firing vessels to be used.

[0055] Calcined granules may be more effective for "cool roof" applications when the granules have a high solar reflectance (SR) value. Without wishing to be bound by a particular theory, it is believed that a high solar reflectance is related to the optical properties of the granules. In particular, a high solar reflectance may correlate to a high Hunter whiteness value and a low Hunter yellowness value.

[0056] The calcined granules may also have a high UV opacity, such as, for example greater than 0.94, 0.95, 0.96, 0.97, or 0.98, as measured according to, for example, the ARMA test method "Measurement of Translucency of Rock Used to Make Roofing Granules." A high UV opacity may also prevent degradation of a roofing material, such as bitumen, to which the calcined granules are adhered.

[0057] The calcined granules may also have high hardness (Mohs hardness). A high hardness may permit the granules to better withstand environmental conditions, such as weather, and other adverse conditions, such as scratches or impacts from, for example, trees, animals, people, ice, or hail. A high hardness may also reduce friability of the granules. Without wishing to be bound by a particular theory, it is believed that friability may increase as a result of crystalline silica being present as respirable crystalline silica resulting from a low hardness. As the hardness of the calcined granules increases, the friability may decrease.
The calcined granules may be adhered to a roofing material, such as bitumen, to improve the properties of the roofing material. A layer of calcined granules adhered to the roofing material may protect the underlying material from degradation and environmental wear. For example, the granules may prevent UV degradation of the underlying material or prevent wear from weather, such as rain, sleet, or hail. The granules may also improve the energy efficiency and thermal properties of the roofing material, for example, by radiating heat away from the roofing material and the building, by preventing the transfer of heat into the building, or by contributing to maintaining a regulated temperature within the building. Coloring may also be added to the granules to improve the aesthetic appearance of the roofing material.

The calcined granules may be adhered to a bituminous roofing material when the bituminous material is soft or deformable. For example, heating a bituminous material to about 150°C may create a soft surface to which the calcined granules may adhere. Additional adhering agents, such as silicone emulsion or mineral oil, may also be used to promote adhesion to a bituminous material.

The calcined granules may also be adhered to the surface of a roofing material using a binding agent. Exemplary binding agents include acrylic emulsions, acrylic solutions, thermoplastic polymers, fluoropolymer emulsions, epoxy resins, UV curable resins, radiation curable resins, alkaline metal silicates, sol-gel solutions, silicone resins, and silica binders. The binding agent may be cured to create a layer containing the cured binding agent and the granules.

Other methods and agents for adhering the granules to a roofing material known to one of skill in the art are contemplated.
[0062] According to some embodiments, the calcined granules are adhered to the surface of the roofing material such that greater than 70% of the surface of the roofing material is covered by the granules. For example, the calcined granules may cover greater than 75%, greater than 80%, greater than 85%, or greater than 90% of the surface of the roofing material.

Example #1

[0063] Samples of kaolin, without a flux, were formed into calcined granules according to the following procedure. 800 grams of hydrous kaolin were added to a small paddle blender and mixed on low speed. 90 grams of water were poured slowly into the blender to a final water concentration of about 10%. The resulting material was mixed in the paddle blender for 30 minutes to ensure homogeneity. The material was then compressed into a tile shape and dried at 80°C for 20 hours. Four samples, A through D, of the material were then fired at 1200°C, 1300°C, 1400°C, and 1500°C, respectively, for 4 hours after a 2.5 hour temperature ramp-up period. The materials were then cooled inside the furnace. The entire calcination cycle lasted approximately 12 hours. Each sample was then crushed using a jaw crusher and a roller mill to obtain a granule size range of 40 mesh (0.4 mm) to 12 mesh (1.68 mm).

[0064] The results of this example are shown in Table 2 below.
TABLE 2

As shown in Table 2, from 1200°C to 1400°C, the calcined kaolin has a relatively low hardness. These low-hardness granules may be insufficient for "cool roof" applications. To obtain a desirable hardness, the temperature must be increased to about 1500°C. Such high firing temperatures may be economically undesirable and may not be easily obtainable in some firing vessels, such as common kilns. Some firing vessels may not be able to achieve temperatures above 1300°C, 1250°C, or even 1200°C. Accordingly, a firing temperature of 1500°C may be unduly expensive or technically difficult to achieve with certain furnaces.

Example #2

According to one embodiment, 800 grams of hydrous kaolin were added to a small paddle blender and mixed on low speed. 114 grams of 37% sodium silicate were added to 209 grams of water and mixed to form a solution. The solution was slowly poured into the blender to a final water concentration of 23%. This composition resulted in about 5wt% sodium silicate relative to the weight of the kaolin. The material was then mixed for 30 minutes to ensure homogeneity. The blended material was extruded via a benchtop ram extruder through a 1/4" circular die. The extruded material was then dried at 80°C for 20 hours. The dried material was then fired at 1200°C for 4 hours after a 2.5 hour ramp-up period. The fired material was then cooled inside the furnace. The entire calcination cycle lasted approximately 12 hours.
The calcined material was crushed via a jaw crusher and a roller mill to a granule size range of 40 mesh (0.4 mm) to 12 mesh (1.68 mm).

[0067] The results of this example are shown in Table 3 below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flux Sodium silicate (%)</th>
<th>Firing Temp (°C)</th>
<th>Whiteness (Hunter, L*)</th>
<th>Hardness (Mohs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>5.0%</td>
<td>1200</td>
<td>93.0</td>
<td>5.5</td>
</tr>
</tbody>
</table>

TABLE 3

[0068] As shown in Table 3, the addition of sodium silicate allowed the calcined granules having desirable properties to be formed at relatively lower temperature, when compared with the samples in Table 2.

Example #3

[0069] A sample of about 15wt% sodium silicate flux was prepared according to the procedure of Example 2, except that 373 grams of 37% sodium silicate were poured slowly into the blender containing the 800 grams hydrous kaolin to a final water composition of 20%. The resulting material was blended, extruded, and dried as described in Example 2, except that the samples were extruded through approximately a 2" die. The dried material was then fired at 1200°C for 4 hours after a 2.5 hour ramp-up period. The fired material was cooled inside the furnace. The entire calcination cycle lasted approximately 12 hours. The sample was crushed via a jaw crusher and a roller mill to a granule size range of 40 mesh (0.4 mm) to 12 mesh (1.68 mm).

[0070] The results of this example are shown in Table 4 below.
TABLE 4

[0071] Comparing Tables 3 and 4, when sodium silicate is added as a flux to the kaolin, high hardness can be achieved at a low firing temperatures, such as 1200°C. When comparing Tables 3 and 4, it appears that as the weight percent of sodium silicate increases relative to the weight of kaolin, the whiteness decreases of the calcined granules and the hardness of the calcined granules increases.

Example 4

[0072] Samples G-J were prepared according to the procedure described in Example 3, except that samples G-J included 5wt%, 7.5wt%, 10wt%, and 12.5wt% sodium silicate, respectively, and were extruded through approximately a 2” die. After blending, extruding, and drying, each of samples G-J was heated at 1250°C for 4 hours after a 2.5 hour ramp-up. The fired material was cooled inside the furnace. The entire calcination cycle lasted approximately 12 hours. The sample was crushed via a jaw crusher and a roller mill to a granule size range of 40 mesh (0.4 mm) to 12 mesh (1.68 mm).

[0073] The results of this example are shown in Table 5 below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flux Sodium silicate (%)</th>
<th>Firing Temp (°C)</th>
<th>Whiteness (Hunter, L*)</th>
<th>SR</th>
<th>Hardness (Mohs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>5.0%</td>
<td>1250</td>
<td>93.5</td>
<td>0.86</td>
<td>2.5</td>
</tr>
<tr>
<td>H</td>
<td>7.5%</td>
<td>1250</td>
<td>94.4</td>
<td>0.85</td>
<td>3.5</td>
</tr>
<tr>
<td>I</td>
<td>10.0%</td>
<td>1250</td>
<td>93.4</td>
<td>0.83</td>
<td>5.5</td>
</tr>
<tr>
<td>J</td>
<td>12.5%</td>
<td>1250</td>
<td>92.3</td>
<td>0.82</td>
<td>7.5</td>
</tr>
</tbody>
</table>

TABLE 5
As shown in Table 5. When sodium silicate is added as a flux before calcination, a high hardness can be achieved for the fired granule at a low firing temperature. When fired at 1250°C, a relatively high Hunter whiteness value, a relatively high solar reflectance value, and a relatively high Mohs hardness value can be achieved by adding between about 10wt% and about 12.5wt% sodium silicate flux.

As shown in Examples 2-4, the addition of a flux, such as sodium silicate, can be used to achieve a high-hardness, high-brightness calcined granule, even when calcination occurs at relatively lower temperatures. The resulting granules can be used, for example, in roofing materials, such as "cool roof" applications.

Example 5

Four samples, K-N, were prepared as described in Example 3, except that the samples included 10.5wt%, 11.2wt%, 11.8wt%, and 12.5wt% flux, and were extruded through approximately a 2" die. The resulting materials were each blended, extruded, and dried. Each sample was then fired at 1200°C for 4 hours after a 2.5 hour ramp-up period. The materials then cooled inside the furnace. The samples were crushed as described in Example 3. A siloxane coating was added to the fired granules.

The results are shown in Table 6 below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flux Sodium Silicate (%)</th>
<th>Firing Temp (°C)</th>
<th>Whiteness (Hunter, L*)</th>
<th>SR</th>
<th>Hardness (Mohs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>10.5</td>
<td>1200</td>
<td>91.6</td>
<td>0.80</td>
<td>4.5</td>
</tr>
<tr>
<td>L</td>
<td>11.2</td>
<td>1200</td>
<td>92.4</td>
<td>0.81</td>
<td>5.5</td>
</tr>
<tr>
<td>M</td>
<td>11.8</td>
<td>1200</td>
<td>92.1</td>
<td>0.81</td>
<td>7.5</td>
</tr>
<tr>
<td>N</td>
<td>12.5</td>
<td>1200</td>
<td>92.7</td>
<td>0.80</td>
<td>7.5</td>
</tr>
</tbody>
</table>

TABLE 6

Example 6
Five samples were prepared by adding potassium feldspar to hydrous kaolin, as described in Example 3, to form samples having 0wt%, 10wt%, 15wt%, 20wt%, and 25wt% potassium feldspar, and were extruded through approximately a 2" die. The final water concentration of about 10%. The resulting materials were each blended, extruded, and dried. Each sample was then fired at 1200°C for 4 hours after a 2.5 hour ramp-up period. The materials were then cooled inside the furnace. The samples were crushed as described in Example 3.

The results are shown in Table 7 below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Flux Potassium Feldspar (%)</th>
<th>Firing Temp CO</th>
<th>Whiteness (Hunter, L*)</th>
<th>Hardness (Mohs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>0%</td>
<td>1200</td>
<td>96.8</td>
<td>2.5</td>
</tr>
<tr>
<td>P</td>
<td>10%</td>
<td>1200</td>
<td>94.4</td>
<td>2.5</td>
</tr>
<tr>
<td>Q</td>
<td>15%</td>
<td>1200</td>
<td>94.8</td>
<td>3.5</td>
</tr>
<tr>
<td>R</td>
<td>20%</td>
<td>1200</td>
<td>93.5</td>
<td>4.5</td>
</tr>
<tr>
<td>S</td>
<td>25%</td>
<td>1200</td>
<td>93.6</td>
<td>5.5</td>
</tr>
</tbody>
</table>

TABLE 7

As shown in Table 7, potassium feldspar can also be used as a flux to prepare high-whiteness, high-solar reflectivity, and high-hardness granules at relatively low firing temperatures. Table 7 suggests that a higher percentage of potassium feldspar may be required to obtain the desired properties for the calcined granules, when compared with the percentage of siloxane or sodium silicate required to achieve a similar high-hardness, high-whiteness material.

As shown in Examples 2-6, the addition of a flux allows the kaolin to be calcined at a lower firing temperature, while still retaining desirable properties such as high-hardness, high-whiteness, and high-solar reflectivity.

Other embodiments of the invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed.
herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.
What is claimed is:

1. A composition comprising:
   an aluminosilicate; and
   a flux,
   wherein the aluminosilicate and the flux are calcined to form calcined granules.

2. The composition of claim 1, wherein the aluminosilicate comprises at least one of kaolin and chamotte.

3. The composition of claim 1, wherein the calcined granules are coated with a hydrophobic coating.

4. The composition of claim 3, wherein the hydrophobic coating comprises a silane.

5. The composition of claim 3, wherein the hydrophobic coating comprises a siloxane.

6. The composition of claim 5, wherein the siloxane comprises at least one siloxane chosen from the group consisting of: dimethylsiloxane, methylphenylsiloxane, methylhydrogen siloxane, methylhydrogen polysiloxane, methyltrimethoxysilane, octamethylcyclotetrasiloxane, hexamethyldisiloxane, octyltriethoxysilane, diphenylsiloxane, and copolymers or blends of copolymers of any combination of
monophenylsiloxane units, diphenylsiloxane units, phenyinnethylsiloxane units, dimethylsiloxane units, monomethylsiloxane units, vinylsiloxane units, phenylvinylsiloxane units, methylvinylsiloxane units, ethylsiloxane units, phenylethylsiloxane units, ethylmethylsiloxane units, ethylvinylsiloxane units, octyltriethoxysilane units, or diethylsiloxane units.

7. The composition of claim 1, wherein the flux comprises a salt.

8. The composition of claim 7, wherein the salt comprises sodium silicate.

9. The composition of claim 1, wherein the flux comprises potassium feldspar.

10. The composition of claim 1, wherein the calcined granules have a hardness greater than 4.5 Mohs.

11. The composition of claim 1, wherein the calcined granules have a hardness greater than 5.0 Mohs.

12. The composition of claim 1, wherein the calcined granules have a hardness greater than 5.5 Mohs.
13. The composition of claim 1, wherein the calcined granules have a hardness greater than 6.0 Mohs.

14. The composition of claim 1, wherein the calcined granules have a hardness greater than 6.5 Mohs.

15. The composition of claim 1, wherein the calcined granules have a hardness greater than 7.0 Mohs.

16. The composition of claim 1, wherein the calcined granules have a hardness greater than 7.5 Mohs.

17. The composition of claim 1, wherein the calcined granules have a whiteness greater than 90.

18. The composition of claim 1, wherein the calcined granules have a whiteness greater than 91.

19. The composition of claim 1, wherein the calcined granules have a whiteness greater than 92.

20. The composition of claim 1, wherein the calcined granules have a whiteness greater than 93.
21. The composition of claim 1, wherein the calcined granules have a whiteness greater than 94.

22. The composition of claim 1, wherein the composition is calcined at a temperature less than or equal to about 1300°C.

23. The composition of claim 1, wherein the composition is calcined at a temperature less than or equal to about 1250°C.

24. The composition of claim 1, wherein the composition is calcined at a temperature less than or equal to about 1200°C.

25. The composition of claim 1, wherein the calcined granules have a solar reflectance of at least 0.80.

26. The composition of claim 1, wherein the calcined granules have a solar reflectance of at least 0.81.

27. The composition of claim 1, wherein the calcined granules have a solar reflectance of at least 0.82.
28. The composition of claim 1, wherein the calcined granules have a solar reflectance of at least 0.83.

29. The composition of claim 1, wherein the calcined granules have a solar reflectance of at least 0.84.

30. The composition of claim 1, wherein the calcined granules have a solar reflectance of at least 0.85.

31. The composition of claim 1, wherein the calcined granules have a solar reflectance of at least 0.86.

32. The composition of claim 8, wherein the amount of sodium silicate comprises less than 15wt% sodium silicate.

33. The composition of claim 8, wherein the amount of sodium silicate comprises between 5wt% and 15wt% sodium silicate.

34. The composition of claim 8, wherein the amount of sodium silicate comprises between 5wt% and 12.5wt% sodium silicate.

35. The composition of claim 8, wherein the amount of sodium silicate comprises between 7.5wt% and 15wt% sodium silicate.
36. The composition of claim 8, wherein the amount of sodium silicate comprises between 7.5wt% and 12.5wt% sodium silicate.

37. The composition of claim 8, wherein the amount of sodium silicate comprises between 7.5wt% and 10wt% sodium silicate.

38. The composition of claim 8, wherein the amount of sodium silicate comprises between 10wt% and 12.5wt% sodium silicate.

39. The composition of claim 9, wherein the amount of potassium feldspar comprises less than 25wt% potassium feldspar.

40. The composition of claim 9, wherein the amount of potassium feldspar comprises less than 20wt% potassium feldspar.

41. The composition of claim 9, wherein the amount of potassium feldspar comprises between 20wt% and 25wt% potassium feldspar.

42. The composition of claim 5, wherein the amount of siloxane relative to the weight of the fired granule comprises at least 0.5wt% siloxane.
43. The composition of claim 5, wherein the amount of siloxane relative to the weight of the fired granule comprises less than 1wt% siloxane.

44. The composition of claim 5, wherein the amount of siloxane relative to the weight of the fired granule comprises less than 0.9wt% siloxane.

45. The composition of claim 5, wherein the amount of siloxane relative to the weight of the fired granule comprises less than 0.8wt% siloxane.

46. The composition of claim 5, wherein the amount of siloxane relative to the weight of the fired granule comprises less than 0.75wt% siloxane.

47. The composition of claim 5, wherein the amount of siloxane relative to the weight of the fired granule comprises less than 0.7wt% siloxane.

48. The composition of claim 5, wherein the amount of siloxane relative to the weight of the fired granule comprises less than 0.65wt% siloxane.

49. The composition of claim 5, wherein the amount of siloxane relative to the weight of the fired granule comprises between 0.5wt% and 0.65wt% siloxane.

50. The composition of claim 1, wherein less than 0.1% of the calcined granules have a granule size greater than 2.36mm.
51. The composition of claim 1, wherein between 4% and 10% of the calcined granules have a granule size less than 2.36mm and greater than 1.7mm.

52. The composition of claim 1, wherein between 30% and 50% of the calcined granules having a granule size less than 1.7mm and greater than 1.18mm.

53. The composition of claim 1, wherein between 10% and 30% of the calcined granules having a granule size less than 850µm and greater than 600µm.

54. The composition of claim 1, wherein between 1% and 10% of the calcined granules having a granule size less than 600µm and greater than 425µm.

55. The composition of claim 1, wherein less than 2% of the calcined granules have a granule size less than 425µm.

56. A method of forming a roofing composition comprising:
   adding a flux to an aluminosilicate to create a mixture, and
   calcining the mixture to form calcined granules.

57. The method of claim 56, wherein the aluminosilicate comprises at least one of kaolin and chamotte.
58. The method of claim 56, further comprising:
coating the calcined granules with a hydrophobic coating.

59. The method of claim 58, wherein the hydrophobic coating comprises a silane.

60. The method of claim 58, wherein the hydrophobic coating comprises a siloxane.

61. The method of claim 60, wherein the siloxane comprises at least one siloxane chosen from the group consisting of: dimethylsiloxane, methylphenylsiloxane, methylhydrogen siloxane, methylhydrogen polysiloxane, methyltrimethoxysilane, octamethylcyclotetrasiloxane, hexamethyldisiloxane, octyltriethoxysilane, diphenylsiloxane, and copolymers or blends of copolymers of any combination of monophenylsiloxane units, diphenylsiloxane units, phenylmethylsiloxane units, dimethylsiloxane units, monomethylsiloxane units, vinylsiloxane units, phenylvinylsiloxane units, methylvinylsiloxane units, ethylsiloxane units, phenylethylsiloxane units, ethylmethylsiloxane units, ethylvinyilsiloxane units, octyltriethoxysilane units, or diethylsiloxane units.

62. The method of claim 56, wherein the flux comprises a salt.
63. The method of claim 62, wherein the salt comprises sodium silicate.

64. The method of claim 56, wherein the flux comprises potassium feldspar.

65. The method of claim 56, wherein the calcined granules have a hardness greater than 4.5 Mohs.

66. The method of claim 56, wherein the calcined granules have a hardness greater than 5.0 Mohs.

67. The method of claim 56, wherein the calcined granules have a hardness greater than 5.5 Mohs.

68. The method of claim 56, wherein the calcined granules have a hardness greater than 6.0 Mohs.

69. The method of claim 56, wherein the calcined granules have a hardness greater than 6.5 Mohs.

70. The method of claim 56, wherein the calcined granules have a hardness greater than 7.0 Mohs.
71. The method of claim 56, wherein the calcined granules have a hardness greater than 7.5 Mohs.

72. The method of claim 56, wherein the calcined granules have a whiteness greater than 90.

73. The method of claim 56, wherein the calcined granules have a whiteness greater than 91.

74. The method of claim 56, wherein the calcined granules have a whiteness greater than 92.

75. The method of claim 56, wherein the calcined granules have a whiteness greater than 93.

76. The method of claim 56, wherein the calcined granules have a whiteness greater than 94.

77. The method of claim 56, wherein calcining the mixture comprises calcining at a temperature less than or equal to about 1300°C.

78. The method of claim 56, wherein calcining the mixture comprises calcining at a temperature less than or equal to about 1250°C.
79. The method of claim 56, wherein calcining the mixture comprises calcining at a temperature less than or equal to about 1200°C.

80. The method of claim 56, wherein the calcined granules have a solar reflectance of at least 0.80.

81. The method of claim 56, wherein the calcined granules have a solar reflectance of at least 0.81.

82. The method of claim 56, wherein the calcined granules have a solar reflectance of at least 0.82.

83. The method of claim 56, wherein the calcined granules have a solar reflectance of at least 0.83.

84. The method of claim 56, wherein the calcined granules have a solar reflectance of at least 0.84.

85. The method of claim 56, wherein the calcined granules have a solar reflectance of at least 0.85.
86. The method of claim 56, wherein the calcined granules have a solar reflectance of at least 0.86.

87. The method of claim 63, wherein the amount of sodium silicate comprises less than 15wt% sodium silicate.

88. The method of claim 63, wherein the amount of sodium silicate comprises between 5wt% and 15wt% sodium silicate.

89. The method of claim 63, wherein the amount of sodium silicate comprises between 5wt% and 12.5wt% sodium silicate.

90. The method of claim 63, wherein the amount of sodium silicate comprises between 7.5wt% and 15wt% sodium silicate.

91. The method of claim 63, wherein the amount of sodium silicate comprises between 7.5wt% and 12.5wt% sodium silicate.

92. The method of claim 63, wherein the amount of sodium silicate comprises between 7.5wt% and 10wt% sodium silicate.

93. The method of claim 63, wherein the amount of sodium silicate comprises between 10wt% and 12.5wt% sodium silicate.
94. The method of claim 64, wherein the amount of potassium feldspar comprises less than 25wt% potassium feldspar.

95. The method of claim 64, wherein the amount of potassium feldspar comprises less than 20wt% potassium feldspar.

96. The method of claim 64, wherein the amount of potassium feldspar comprises between 20wt% and 25wt% potassium feldspar.

97. The method of claim 60, wherein the amount of siloxane relative to the weight of the fired granule comprises at least 0.5wt% siloxane.

98. The method of claim 60, wherein the amount of siloxane relative to the weight of the fired granule comprises less than 1wt% siloxane.

99. The method of claim 60, wherein the amount of siloxane relative to the weight of the fired granule comprises less than 0.9wt% siloxane.

100. The method of claim 60, wherein the amount of siloxane relative to the weight of the fired granule comprises less than 0.8wt% siloxane.
101. The method of claim 0, wherein the amount of siloxane relative to the weight of the fired granule comprises less than 0.75wt% siloxane.

102. The method of claim 60, wherein the amount of siloxane relative to the weight of the fired granule comprises less than 0.7wt% siloxane.

103. The method of claim 60, wherein the amount of siloxane relative to the weight of the fired granule comprises less than 0.65wt% siloxane.

104. The method of claim 60, wherein the amount of siloxane relative to the weight of the fired granule comprises between 0.5wt% and 0.65wt% siloxane.

105. The method of claim 56, wherein less than 0.1% of the calcined granules have a granule size greater than 2.36mm.

106. The method of claim 56, wherein between 4% and 10% of the calcined granules have a granule size less than 2.36mm and greater than 1.7mm.

107. The method of claim 56, wherein between 30% and 50% of the calcined granules have a granule size less than 1.7mm and greater than 1.18mm.

108. The method of claim 56, wherein between 10% and 30% of the calcined granules have a granule size less than 850\(\mu\text{m}\) and greater than 600\(\mu\text{m}\).
109. The method of claim 56, wherein between 1% and 10% of the calcined granules have a granule size less than 600\(\mu\)m and greater than 425\(\mu\)m.

110. The method of claim 56, wherein less than 2% of the calcined granules have a granule size less than 425\(\mu\)m.

111. The method of claim 56, further comprising:
adding the calcined granules to a roofing material.

112. The method of claim 111, wherein the roofing material comprises bitumen.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - D06N 7/04 (2015.01)
CPC - G03B21/62; G02B5/128; B05D5/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC(8); D06N 7/04 (2015.01)
CPC: G03B21/62; G02B5/128; B05D5/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

CPC: B24D3/04; B24D18/00; C04B35/00; C04B35/1 115 (keywords limited; search terms below)
USPC: 51/308; 428/402 (keywords limited; search terms below)

Electronic database consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST (PGPB; USPT; EPAB; JPAB); PatBase; Google Scholar; Google Patents
Search terms: aluminosilicate$2 flux calcins$6 granul$7 roofing granules$2 silane$2 siloxane$2 “sodium silicate” “potassium feldspar” hardness reflectance “granule size” “particle size” hydrophobic dimethyldisiloxane temperature

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 201 1/006201 A1 (Shiao et al.) 14 April 2001 (14.04.2001 1), especially, Table 6, para [0003], [0008], [0014], [0015], [0021], [0049], [0060], [0080], [0081] and [0104].</td>
<td>1, 2, 7, 8, 22-31, 50-57, 62, 63, 77-86, 105-112</td>
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<td>Y</td>
<td>US 2008/026183 A1 (Vanpouille et al.) 31 January 2008 (31.01.2008), especially, para [0018], [0073], [0080], [0081], [0100] and [0101].</td>
<td>3-6, 9-21, 32-49, 58-61, 64-76, 87-104</td>
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<tr>
<td>Y</td>
<td>US 2002/006233 A1 (McArdle et al.) 6 June 2002 (06.06.2002), especially, para [0002], [0034], [0057], [0061] and [0064].</td>
<td>9-16, 39-41, 64-71, 94-96</td>
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<td>Y</td>
<td>US 2012/0288678 A1 (Grube et al.) 15 November 2012 (15.11.2012), especially, para [0013] and [0014].</td>
<td>17-21, 72-76</td>
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<tr>
<td>Y</td>
<td>US 2013/029717 A1 (Edwards et al.) 15 August 2013 (15.08.2013), especially, para [0017] and [0056].</td>
<td>32-38, 87-93</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

Date of the actual completion of the international search: 27 March 2015 (27.03.2015)  
Date of mailing of the international search report: 09 April 2015 (09 APR 2015)

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