The following statement is a full description of this invention, including the best method of performing it known to us:

METHOD FOR MANUFACTURE OF MAGNESIA

Related Art (56)

431881 (48819/69) 04.1; 06.7; 19.2
406514 (66482/65) 19.2
290001 (49747/64) 04.1; 19.4; 19.2
This invention relates to methods of preparing electrical grade magnesia.

In the making of shaped electrical resistance elements such as the spiral heater elements on a domestic electric stove, a resistance wire is centered in a substantially straight tube with fused magnesia insulating grain separating the wire from the tube which is then rolled or swaged to reduce the tube to its final size and cross-section. The metal after being worked in this manner must be annealed by a heat treating step to facilitate subsequent bending, and after the composite tube structure is heated the partially shaped tube may then be bent to its final form such as a spiral shape for a burner or square shape for a bake and broil unit, for example. The magnesia insulating grain must flow evenly during the several bending steps that are performed in order to remain in its proper position between the inside tube wall and the wire to hold them apart and therefore the sintering properties of the magnesia are important. If the fused magnesia insulating grain or powder should sinter to any degree during the heating step performed to anneal the tube at the intermediate stage of its formation, a brittle magnesia envelope would be formed around the wire within the tube, which sintered envelope would not flow during the subsequent bending operation.
If this should happen a satisfactory heating element cannot be formed.

A magnesia which can perform satisfactorily in such a process is for the purposes of this application described as an electrical grade magnesia.

Magnesia sources relatively high in boron content have been found to be of little use for electrical purposes because boron acts as a sintering aid. Magnesia having more than about 125 ppm of boron sinters unduly at the temperatures used for annealing the metal and the free flowing powdery or granular characteristic of the magnesia is lost. Thus the cheap brine or sea water magnesite containing a relatively high boron content in the range of 200 ppm and higher as compared with India magnesite, or that extracted from dolomite, cannot be used for the making of electrical heater elements which must be rolled, swaged or otherwise worked and then heat treated to be annealed prior to being bent to final form because the fused magnesia from the sea water source or any other similar boron containing magnesia, would sinter to a detrimental extent during annealing. Such formed composite metal-magnesia electrical elements are manufactured in vast quantities for use in domestic appliances, as above indicated or may be made for use in industrial electrical resistance heater applications and have heretofore required the use of a relatively expensive boron free magnesia component to permit the necessary annealing step to be performed.

It has now been found, however, that a magnesite having a relatively high boron content i.e. above 200 ppm
can be chemically reacted with titania, zirconia or in some instances alumina to prevent substantially in most instances the boron from acting as a sintering aid. When so reacted, a fused magnesia containing even as much as 300 parts per million of boron can be used for electrical insulation purposes in metal constructions that are subjected to several shaping operations wherein a composite metal and magnesia structure must be heated together to anneal the metal to condition the metal element used for example in the making of spiral or other shaped electrical resistor elements for the final bending operation in the manufacture of such an intricately shaped element. If a magnesia having a high sinter index is used in the making of such an element, that must be annealed, a brittle sintered magnesia forms within the metal element, which interferes with the subsequent bending operations that must be performed on the metal to produce the final shape desired.

According to the invention therefor there is provided a method of preparing a fused electrical grade magnesia product from a magnesia containing amounts of boron detrimental to the properties in annealing wherein the magnesia as fused grain is combined with finely ground material containing principally at least one of titania, alumina, or zirconia in from 1/2 to 7% by weight of magnesia and the mixture is calcined at from 950° to 1275°C.

Fused magnesia produced from a more purified brine or sea water magnesite, having from 200 to 300 parts per million of boron and fused magnesia from other less purified sea water sources of magnesia, having up to
as much as 1500 to 3000 parts per million of boron have been successfully treated to drastically reduce the activity of the boron in the fused crushed magnesia insofar as it acts as a sintering aid. As much as 7% by weight of a commercially pure zirconia has been added to such fused, crushed magnesia material of 40 Tyler mesh and finer and the mixture calcined at a temperature in the range of 1000°C. to react the zirconia with the boron. The zirconia is preferably introduced into a mixture with sea water or brine magnesia having up to 300 parts per million of boron, that has been fused and finely ground to 325 mesh and finer on the Tyler screens. The mixture is then calcined at a temperature controlled so that it does not go over about 1275°C., at which temperature the boron-zirconia compound becomes unstable. The resulting granular fused magnesia and zirconia product after calcination is then ready for use as the insulating element in a resistor element, and deleterious sintering of the magnesia material upon subsequent heating to anneal the metal during further processing of the composite resistor element will usually not be encountered.

Commercial sea water magnesia was secured as produced by the Standard Lime and Refractory Company which upon analysis after fusion in a conventional process was found to contain 300 parts per million of boron. For electrical insulation purposes, without the present treatment, an excess of about 125 parts per million of boron in such fused, crushed magnesia was intolerable. When more than this amount of boron is present, the sinter index increases very rapidly and is in fact relatively
uncontrollable to such an extent as to render any such material useless for electrical insulation purposes in the making of a conventional bent to shape resistor element. Typical Sinter Indices in grams for fused, crushed sea water magnesite products calcined at different temperatures are as follows:

**TABLE I**

<table>
<thead>
<tr>
<th>Boron Level</th>
<th>Sinter Temperature</th>
<th>Sinter Index (grams)</th>
</tr>
</thead>
<tbody>
<tr>
<td>182ppm</td>
<td>1100°C, 1275°C</td>
<td>438</td>
</tr>
<tr>
<td>760-790ppm</td>
<td>1100°C, 1275°C</td>
<td>590</td>
</tr>
<tr>
<td>1240-1440ppm</td>
<td>1100°C, 1275°C</td>
<td>1364</td>
</tr>
</tbody>
</table>

Sinter index as used in this description is determined in accordance with the final draft of the "Proposed Standard Method for Measure of the Degree of Sinter of Electrical Grade Magnesium Oxide for use in Sheathed Type Electric Heating Elements", published on March 31, 1970 by the American Society for Testing Materials.

**EXAMPLE**

Fused sea water magnesia having 220 ppm of boron, was crushed to pass through screens of 40 Tyler mesh size and smaller down to 425 mesh and the crushed magnesia was intimately mixed with 2% by weight of pure zirconia either fused or unfused and ground to minus 325 mesh U.S. Standard Screen size. The resulting mixture was calcined under static conditions in an oven for one hour at a temperature of 1025°C. The reacted calcined product was found to have a sinter index of 85 grams as compared with an index of 320 grams when no zirconia is added and...
the same magnesia is calcined at 1025°C. for one hour.

A second mixture of a ground zirconia containing material with a batch of the same fused, crushed sea water magnesite was made and calcined as above described except that 2% by weight of a fused zircon sand was crushed to under 325 mesh size and added to the magnesite having 220 parts per million of boron. After sintering for one hour at 1025°C., the resulting product had a sinter index of 166 grams as compared with 320 grams for the unmixed magnesite.

While a sinter index of 150 grams is preferred as a target for fused magnesia that is to be used for electrical insulation, a sinter index of 166 grams is tolerable when the boron in the magnesite is controlled as taught herein because the sinter index increases very gradually in a controlled manner when the boron is reacted as here taught to minimize its sintering aid characteristic.

An addition of finely crushed to 325 mesh and finer Al₂O₃ fused zircon where the ZrO₂ was present in an amount equal to 70% by weight of the composition, was added to the above mentioned fused, crushed sea water magnesia and calcined for one hour at 1025°C. The Al₂O₃ zircon composition was added in an amount equal to 2% by weight of the magnesia and the resulting product had a sinter index of 101 grams.

A 325 mesh and finer magnesium zirconate was added to the same fused, crushed magnesia at the 2% by weight level and after calcination at 1025°C. for one hour a product was produced having a sinter index of 122 grams.
Al₂O₃ was added in the amount of 2% by weight to the same fused, crushed magnesia and upon calcination at 1025°C. for one hour the final product had a sinter index of 287 grams which may be too high for use as an electrical insulation in known sheathed and bent to shape resistor elements, but other uses for such a fused sea water magnesia-alumina material having a somewhat reduced sinter index may be found.

With a 2% alumina addition to the same fused, crushed magnesite, when the mix was calcined at a temperature of 1100°C. for one hour the magnesite was reacted to produce a material having a sinter index of 243 grams. However, when higher calcining temperatures in the range of 1275°C. are used, alumina as an additive in the 2% to 4% range produces, proportionately, a more substantial reduction of the sinter index in the magnesia having a high boron content as compared with a similar addition and sintering procedure where the alumina is added to a magnesia having a lower boron content.

In another example 3% of Al₂O₃ by weight was mixed in finely divided form (i.e. under 325 mesh) with the same fused, crushed sea water magnesia. When such mixture was calcined at 1100°C. for one hour the resulting material was found to have a sinter index of 103 grams which was well within the useful sinter index range of 150 grams that has been found to be practical for the making of conventional metal sheathed electrical resistor elements.

At the 3% by weight level and 1100°C. calcination for one hour under static conditions, a zirconia addition
of 325 mesh and finer to the same fused, crushed sea water magnesia produced a product with a sinter index of 42 grams, fused, crushed zircon of the 325 mesh size and finer produced a sinter index of 124 grams, a fused, crushed alumina zircon (70% ZrO₂ by weight), 325 mesh and finer addition produced a 151 gram sinter index and an addition of a fused, crushed material 325 mesh and finer containing alumina (10%), silica (5%), zirconia (85%) (all percentages by weight) produced a sinter index of 131 grams.

A fused, crushed sea water magnesite having 182 parts per million of boron was found to have a sinter index of 525 gms. When a titania addition of 1% by weight of 325 mesh and finer was mixed with this magnesite and calcined at 1100°C. for one hour the sinter index was found to be 258 gms. A 2% by weight addition calcined at 1100°C. for one hour reduced the sinter index to 130 gms. With a 6% by weight titania addition and calcination for one hour at 1100°C. the sinter index was found to be 137 gms.

In all of the examples described above the alumina, titania or zirconia containing material was crushed to pass through a 325 mesh Tyler screen before mixing with the fused, crushed sea water magnesia ground to 40 mesh and finer on the Tyler screens. The finer the additive material is crushed, the more it may be dispersed throughout the magnesia to react more readily with the boron present to tie up the boron whereby to minimize its activity as a sintering aid for the magnesia. Pure zirconia as an addition product is preferred but pure...
titania and pure alumina can be found to have value for this purpose as well as fused alumina, zirconia materials fused zircon and magnesium zirconate.

The reaction that takes place between the boron and the addition agent, may be performed under static conditions in the range of about from 950°C. to 1275°C. Preferably the calcination is performed under such static conditions for one hour at a temperature in the range of between 990°C. to 1100°C. If the temperature is too high the boron reaction product appears to be unstable and the desired result is not obtained.

If calcination is performed in a rotary kiln the reaction can be speeded up.

Zirconia additions have been made to fused, crushed sea water magnesia having a boron content of 1820 parts per million. At a 1% by weight addition of 325 mesh and finer ZrO₂ and static calcination for one hour at 1025°C., the resulting product had a sinter index of approximately 3700 grams. With a 4% addition the sinter index dropped to about 1600 grams, with 5% to a sinter index of 1400 grams and at 6% to a sinter index of just below 800 grams. While this treated material was not useful for insulation in a sheathed resistor element of spiral shape for example, the very great decrease in the sinter index, demonstrates the serviceability of the procedure for reducing the sintering aid activity of boron in the fused, crushed sea water magnesia sample used.

The product resulting from the process of the invention will be found generally to have good resistivity
characteristics and while it may not be useful for all of the applications for electrical magnesia it has excellent properties for all normal low temperature applications of such material for example where an intermediate heating or sintering step is performed upon a composite structure prior to final shaping and to this extent may also be described as electrical grade magnesia.
The claims defining the invention are as follows:

1. A method of preparing a fused electrical grade magnesia product from a magnesia containing amounts of boron detrimental to the properties in annealing wherein the magnesia as fused grain is combined with finely ground material containing principally at least one of titania, alumina, or zirconia in from 1/2 to 7% by weight of magnesia and the mixture is calcined at from 950° to 1275°C.

2. A method according to claim 1, wherein the finely ground material is at least one of titania, alumina, zirconia, fused zircon, fused alumina-zirconia, magnesium zirconate.

3. A method according to either of claims 1 and 2, wherein the calcination is at from 990° to 1100°C. for 1 hour.

4. A method according to any one of claims 1 to 3, wherein the finely ground material is under 325 mesh (Tyler screen) in size.

5. A method according to any one of claims 1 to 4, wherein the magnesia is sea water magnesite containing approximately 300 parts per million of boron.

6. A method of preparing a fused electrical grade magnesia substantially as hereinbefore described in the Examples.
7. A method according to any one of claims 1 to 5, wherein the calcined product is filled into a straight metal tube to surround a resistance element to hold it spaced from the inside wall of the tube and the tube is swaged, annealed and bent to produce a sheathed electrical element.

8. A fused electrical grade magnesia when produced by a method according to any one of claims 1 to 6.

9. A sheathed electrical element when produced by a method according to claim 7.

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