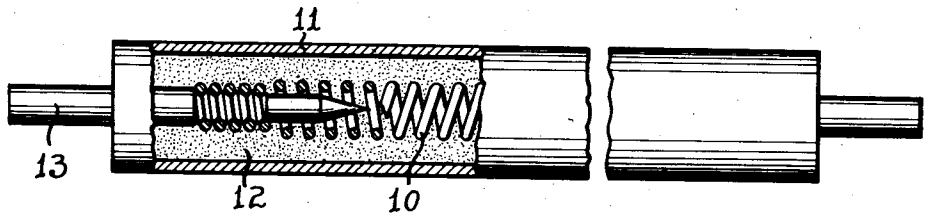
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ELECTRICAL INSULATING MATERIAL AND METHOD OF PRODUCING THE SAME

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ELECTRICAL INSULATING MATERIAL AND METHOD OF PRODUCING THE SAME

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This invention relates to electric heaters and an insulating material therefor and to a method of making the same, and more specifically to an insulating material comprising magnesia having such refractory and resistivity characteristics as adapt it for use as an insulation for high temperature apparatus.

Owing to its refractory nature, as well as its property of being a non-conductor of electricity at high temperatures, magnesia has been found well adapted for use as in insulation in an electric heating unit, which may comprise a resistance wire enclosed within a metallic sheath and embedded in and separated from the sheath by the insulating powder. It is desirable in many such constructions that the electrical insulation be of a minimum thickness between the resistance wire and the outer metal sheath, because of the fact that any refractory powder is a heat insulator to some extent, so that a temperature gradient exists between the resistor wire and the sheath. Since the highest permissible operating temperature of the wire is fixed, the insulating value of the magnesia powder places definite limitations on the power density of the resistor and the external operating temperature of the heating unit. It is, therefore, desirable to provide an electrical insulating medium having a high specific resistance at elevated temperatures, so that a small thickness of the resistance medium will maintain the required protection against grounding of the heating element while permitting the maximum heat flow from the resistor to the outer sheath.

Crystalline magnesia or periclase may be prepared from magnesite ore by calcination and fusion thereof and crystallization in an ingot. It has been considered heretofore that the calcium oxide, silica and free alkalis commonly found in crystalline product were highly detrimental, and that to give good results at high temperatures the magnesia should be substantially free from these impurities. It has also been proposed to roast the magnesia in either a reducing or an oxidizing atmosphere and then slowly cool it to increase its resistivity and stability in the presence of moisture. We have, however, found that such insulating material as has been heretofore made and treated may have a high initial resistance, but that the protective value of the magnesium oxide decreases gradually throughout the use of the heating element. Also, in accordance with out discoveries, we have found that it is the iron oxide and not the silica or lime in the crystallized magnesia which causes this deterioration in the insulating properties of the heating unit.

It is, accordingly, the primary object of our invention to provide an insulating material which will not deteriorate rapidly when used at a high temperature and which will maintain its electrical insulating properties throughout a long period of time and use.

A further object is to provide a resistance heating unit which may give a high rate of heat flow from the inner resistor to the outer sheath and which permits the resistance element to be operated at a very high temperature within the requirements of its own particular characteristics without serious deterioration of the magnesia insulation for a long time.

A further object is to provide a method of making an insulating material comprising magnesia which will be well adapted for insulating purposes at a high temperature. Further objects will be apparent in the following disclosure.

We have discovered that iron in either the metallic form or as an oxide is detrimental in an insulating material made of crystalline magnesia and that the mere conversion of any iron impurity in the magnesia to iron oxide does not result in a satisfactory insulating material. If the magnesia contains more than about 0.1% by weight of iron oxide, the initial high resistance of the magnesia at a standard high operating temperature is gradually decreased throughout the use of the element; and it is desirable to maintain the iron oxide content less than this percentage irrespective of the quantity of alkaline earth or alkali metal compound that may be present.

We also propose that such iron oxide as remains in the magnesia be in the ferric oxide form which is not readily reduced to metallic iron by hydrogen under the temperature conditions maintained. It is believed that residual or absorbed water in the magnesium oxide is electrolyzed, due to a slight rectification of the alternating current in the heating unit, with a resultant production of hydrogen which is capable of reducing the lower oxide of iron to the metallic form and thus provides a conducting material within the insulating body.

We have further found that when the iron content is controlled as herein defined, the silica gives beneficial effects. For example, a magnesia insulating material having an electrical resistivity of 7.8 megohms per inch cube was improved by the addition of 1% of silica which gave a resistivity of 20.8 meghoms. Also, the lime com-

monly associated with magnesia tends to cause disintegration of the magnesia crystals and swelling of the heating unit, but this is prevented by the presence of silica which presumably forms a stable compound therewith. We accordingly use crystalline magnesia, containing preferably not over about 0.1% of iron, calculated as ferric oxide, which has a content of 0.5 to 3.0% by weight of lime and 0.3 to 5% of silica. The preferred maximum limits are 2.5% of lime and 3.0% of silica. Since the material is fused at a high temperature, it is presumed that the impurities in the final product are present in some combined form, but they are referred to herein as the oxides, whether they exist separately or combined.

Hence, in accordance with our invention, we provide an insulating medium comprising magnesia in crystalline and powdered form which contains silica and lime within the above limits, and which is free from metallic iron and preferably contains less than 0.1% by weight of iron oxide, and wherein that iron oxide is in the form of ferric oxide. Moreover, the ferric oxide is preferably absorbed within the magnesia crystal and does not exist as a free phase, so that it may not be readily reduced by hydrogen under the temperature conditions prevailing during the use and heating of the unit.

We may select commercial magnesite ore which has initially less than 0.2% of iron in the form of oxide or metal, or we may use a lower grade of ore, but preferably one containing not over 0.5% by weight of iron oxide and upwards of 95% by weight of MgO, since the following procedure will serve to remove the reducible material from the magnesia.

The selected magnesite is carefully handled to avoid contamination with any iron in the processes of treatment, including shipping, crushing and storing. It may be held in paper bags or wooden containers rather than in steel containers, inasmuch as the addition of even a slight amount of iron in any form is highly objectionable. Prior to furnacing the ore, it is crushed and preferably by means of apparatus which introduces the minimum of iron. Then the crushed material is run through a high intensity magnetic separator of well known form to remove any iron or magnetic iron oxide that may be thus removable.

The magnesite ore is fused in a Higgins furnace or other open top electric arc furnace employing electrodes, such as those made of graphite, which are free from iron. The furnace walls are also made of a material, such as magnesia bricks or some of the crystallized refused magnesia, which will not add iron to the bath. The electric furnace is operated generally according to standard practice, but we maintain a high power input per unit volume of the liquid magnesia resistor, so that a temperature above 2600° C. is reached. At this temperature, there is a tendency for any metallic iron that may be present to boil off and outwardly from the open top of the furnace. The powdered magnesia is fed continuously or periodically into the top of the furnace and the electrodes are raised as required to keep them properly positioned relative to the rising level of liquid magnesia so as to maintain the needed power input for the fusion step.

The fused mass of magnesia is allowed to cool slowly and to crystallize within the furnace, and thereafter it is removed from the furnace shell and further cooling effected. After the ingot is cold, it is broken into large lumps and the outer zone and the extreme center or pipe of the ingot are removed and discarded. The outer area is found to be slightly richer in iron content than the intermediate portion. Also, the lower melting impurities, such as the lime and silica, tend to concentrate in the central pipe, which is the last portion of the ingot to cool and crystallize. By this special selection, the final product is reduced in its lime and silica content as well, if their amounts are too high.

The selected zone of material is crushed in such a manner as to avoid contamination with additional iron insofar as possible. The iron which is still present as a contamination in the magnesia is largely the metal and the magnetic oxide and, therefore, capable of being separated in a high intensity magnetic separator. Consequently, the magnesia ingot, after it has been crushed, is again passed through a high intensity magnetic separator to remove the available traces of metallic iron or Fe_3O_4.

Since the iron content is present partly as metallic iron or a lower oxide, the purified magnesia powder is roasted under oxidizing conditions at a suitable temperature, such as from 1200 to 1400° C., for a period of 24 to 72 hours, and preferably at a temperature above 1250° C. for not less than 48 hours. The magnesia is preferably in the condition of a powder which will go through a screen of 40 meshes per linear inch and be retained by a screen of 325 meshes. This roasting operation is believed to result in a recrystallization of the fine sizes of magnesia, and it serves to improve the electrical resistivity of the magnesia to a material extent. This roasting operation is carried on with an excess of air present so as to oxidize to the higher oxide Fe_2O_3 any metallic iron or lower oxide of iron that may be exposed. This higher oxide is less easily reduced to metallic iron than are the lower oxides during the subsequent use of the powder in an electric resistance heating unit. We have assumed, without proof, that by holding the magnesia grain at a high temperature for a long time we have caused the iron to combine with the magnesia crystals in some form. A possible explanation is that a spinel of the composition of $MgO.Fe_2O_3$ is formed by the prolonged heating, and that this spinel is isomorphous with the magnesia crystals and so enters into solid solution therewith and results in a uniform distribution of iron throughout the crystalline magnesia phase. Hence, it is not necessary to purify the magnesia to the extent of eliminating all of its iron content, since the insulating properties of the material may be greatly enhanced and the useful life thereof prolonged by so treating the material as to insure that the iron content is present in the oxidized condition but is absorbed or dissolved in or dispersed throughout the magnesia crystal and does not exist as a free phase external of the individual magnesia crystals where it may be reduced to iron or otherwise develop conducting paths between the resistance wire and the surrounding metallic sheath of a heating unit.

The roasted material may then be cooled in accordance with standard practice or by a rapid chilling or quenching step, as set forth and claimed in our copending application Serial No. 301,643 filed on even date herewith. Care should be taken at all times to avoid undesired contamination and particularly to insure that the material does not contain over 0.1% of a free

phase of ferric oxide. The crystalline magnesia made according to the above procedure usually contains less than 0.1% by weight of iron oxide.

The accompanying drawing is a view, partly broken away, of a simple form of heating unit embodying this invention. The structure comprises a helically coiled metal resistance wire 10 located centrally within a metal sheath or casing 11 and supported by the special insulating material 12 as above described. An electric terminal 13 may be suitably secured to the resistance wire at each end thereof and similarly insulated from the casing by the material 12. Any suitable structure may, however, be employed.

Hence, by means of this material, we have provided a new electric heating unit having a resistance wire embedded in and insulated from a support, such as a metal sheath, by means of a refractory insulating material consisting chiefly of crystalline magnesia, which is substantially free from iron in any form and in which the slight amount of iron impurity remaining in the material is preferably dissolved within the magnesia crystal in the form of ferric oxide which is not easily reduced to the metal during use of the unit. If this freedom from detrimental iron is maintained, then we may use a magnesia insulation having the calcium and silicon contents, calculated as oxides, as high as 5% by weight of silica and 3.0% of calcium oxide. We prefer to maintain the proportions within the lower limits of 0.5 to 2.5% of CaO and 0.3 to 3.0% of SiO_2. These limits permit the electrical resistance unit to be used under standard conditions at a temperature as high as 1000° C. without the unit showing any serious deterioration in insulating quality over a period of 5000 hours. In other words, the magnesia as thus prepared has a high dielectric strength and stability in its electrical insulating properties, and the unit will not break down before the resistance wire has given a long life of useful service. Because of such properties, the insulation surrounding the wire may be very thin and thus offer but little resistance to the conduction of heat therethrough.

It will now be appreciated that many variations may be made in the method of procedure and that the product may have wide variations in composition provided any free phase containing iron is present as ferric oxide and the total amount of any iron compound present is not over about 0.1% by weight, calculated as ferric oxide, and provided the silica and lime are held within the limits above defined. Also, the material may be used in a wide variety of types of apparatus and for many purposes. Hence, the above disclosure is to be considered as illustrating the general principles and certain embodiments of the invention and methods of procedure but is not to be viewed as a limitation upon the invention except as the latter is defined by the claims appended hereto.

We claim:

1. The method of making an electrical heating unit insulating material comprising the steps of providing magnesia containing compounds of iron, silicon and calcium in amounts, calculated as oxides, of not over 0.5% by weight of ferric oxide, 5% of SiO_2 and 3% of CaO, melting and crystallizing the magnesia of the material, reducing the iron content during the treatment of the material to a total of not over about 0.1% by weight, calculated as ferric oxide, and roasting the material in a granular condition in an oxidizing atmosphere for at least 24 hours at a temperature above 1250° C. and thereafter cooling the same.

2. The method of making an electrical heating unit insulating material comprising the steps of melting and crystallizing magnesia and providing a crystalline material which in the final product contains compounds of iron, silicon and calcium in amounts, calculated as oxides, of not over 0.1% by weight of ferric oxide, 0.3 to 5% of SiO_2 and 0.5 to 3% of CaO, roasting the crystalline material in a granular condition in an oxidizing atmosphere at a temperature between 1250° C. and 1400° C. for at least 24 hours to insure that the iron compound is present substantially wholly as ferric oxide and thereafter cooling the material.

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