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2,809,137

**INSULATING COATING FOR MAGNETIC SHEET MATERIAL AND METHOD OF MAKING THE SAME**

John Cornelius Robinson, deceased, late of Pittsfield, Mass., by Gladys Robinson, administratrix, Pittsfield, Mass., assignor to General Electric Company, a corporation of New York

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The present invention relates to coated metallic sheet materials and the method of making the same.

More particularly, the invention concerns a refractory coating material which can be applied to magnetic sheet materials to prevent adherence to each other when subjected to heat treatment in multi-ply assembly and which serves as a permanent insulating coating in the use of the metallic sheet material in laminated electrical structures.

The forms of magnetic sheet material with which the invention is concerned include strip material such as used in wound transformer cores, and cut or punched laminations forming stacked transformer cores and other electrical apparatus. Examples of compositions of magnetic sheet materials which may be effectively coated in accordance with the invention are nickel-iron alloys, silicon steel, common iron and other ferromagnetic materials.

In the process of treating the magnetic sheet materials to adapt them for use in transformers or other electrical devices, the sheet material is generally wound in the form of a roll or cut and arranged into a plurality of stacked sheets, and placed in these forms in an annealing furnace for the purpose of developing the magnetic properties of the sheet material. During the heat treatment in the furnace with the sheet material either in wound or stacked form, the adjacent surfaces of the magnetic sheet material are in contact with each other over comparatively large areas with the result that at the elevated temperatures employed for developing the magnetic qualities of the material, the adjacent laminations or turns of the material tend to stick together unless some means is provided for separating the surfaces during the heat treatment.

Further it is desirable for an insulating barrier to be provided between the adjacent laminated sheets of the magnetic material in order to reduce the eddy current loss in the core formed by the sheet material in its use in a transformer, motor, or the like.

It is an object of the present invention to provide an improved coating for magnetic strip or sheet material to serve as a separator coating for the sheet material in stacked or wound form during heat treatment and also as a permanent insulating film.

A further object of the invention is to provide an improved separator and insulating coating on metallic sheet material without the aid of a supplementary binder substance.

Still another object of the invention is the provision of an improved process of providing a coating of the above type on magnetic sheet materials.

The above objects and advantages, and others which will become apparent from the following description of the invention, have been attained by applying to the surface of metallic sheet material a suspension of a finely divided inorganic refractory material consisting essentially of colloidal silica of a particular type and at least one refractory oxide, drying the thus applied suspension so as to form a refractory coating on the surface of the sheet material, and annealing the thus coated sheet material

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in multi-ply assembly with the refractory coating separating adjacent surfaces of the sheet material, so as to form a permanent, tightly adherent, electrically insulating layer of refractory material on the surface of the metallic sheet material.

In the past, various types of refractory materials have been used as separator coatings for the wound or stacked metallic sheet material, but these materials due to their nature could not be used as permanent insulating coatings after anneal for the reason that they did not form an intimately bonded, tightly adherent layer on the metal surface even during the annealing process and could therefore be easily wiped off by contact. Even when special binders were used to make the refractory substance adhere to the metal surfaces before anneal, these binders decomposed under the annealing temperature and the refractory particles became separated from the metal surface, so as to be easily rubbed off thereafter.

In the Robinson Patent No. 2,641,556, assigned to the same assignee as the present application, a methyl cellulose binder was disclosed which, when mixed with a refractory material such as magnesia, formed a relatively permanent insulating coating on the surfaces of metallic sheet materials subjected to annealing treatment. In effect, the methyl cellulose served as a wetting agent to aid in securing an inorganic coating to the surface of magnetic steels prior to heat treatment.

It has been discovered, however, in accordance with the present invention that a particular type of refractory material may be used without the methyl cellulose or other special binder to form a tightly adherent insulating layer on the metal sheet material which remains permanently after the heat treatment. This refractory material is a colloidal silica having unique properties which enable such permanent coatings to be formed, and so far as can be determined, no other refractory material, or even silica in other forms is capable of giving similar results.

The colloidal silica material which has been found effective is of such nature and in such a finely divided state that it comes into extremely intimate adherence with the surface of the steel, with the result that during the heat treatment the magnesia component of the present coating composition, the colloidal silica and the steel surface participate in a chemical combination, without the coincident presence of a sticking or binding agent such as the methyl cellulose described above.

Two principal properties of the colloidal silica thus appear to be involved. First, the physical form of the colloidal silica, when dried, has the property of knitting together the magnesia or other ingredients of the coating and assisting in bonding it to the surface of the steel. The second factor is the minute state of subdivision of the colloidal silica, which makes an almost molecular distribution of the material throughout the magnesia so as to give best opportunity for chemical reaction during the annealing process.

A colloidal silica having the above properties and found particularly suitable for the present invention is commercially available under the name of "Ludox" and is a product of E. I. du Pont de Nemours and Company. This product has the following approximate chemical composition and properties:

SiO <sub>2</sub> -----	29-31%.
Na <sub>2</sub> O-----	31-41%.
Sulfates as Na <sub>2</sub> SO <sub>4</sub> -----	.15% maximum.
pH-----	9.5-10.5.
Specific gravity ° Bé-----	24.7-26.4°.
Viscosity at 25° C-----	2.0-3.3 cps.
Freezing point-----	32° F. (silica irreversibly precipitated).

This colloidal silica which is an aqueous solution con-

taining the SiO<sub>2</sub> in an extremely finely divided form is made by an ion exchange technique. The basic material used in the manufacture is sodium silicate, and the final colloidal silica composition contains an SiO<sub>2</sub>:NaO<sub>2</sub> ratio of 75-95:1.

The process for producing the colloidal silica particles involves the condensation of silicic acid molecules to form highly cross-linked micelles. These ultimate particles are spherical in nature, as has been established by electron micrographs. At 25,000 magnification, the ultimate particles are still so small that definition under such a microscope is only fair. It is estimated that the range of particle size in this colloidal silica is from 10-30 millimicrons. The average colloidal silica micelle finally obtained contains about 33,000 silica nuclei.

This colloidal silica composition is miscible in all proportions with water and its stability is increased by dilution, and for these reasons it is possible to produce the slurries necessary for application of inorganic coatings to steel without altering the physical and chemical condition of the silica. The structure of the dried colloidal silica is such, as noted above, as to bind together the magnesia refractory powder and bind the whole to the steel surface. The dried product is insoluble in water, and in this way offers some resistance to natural atmospheric moisture.

Other applications which have involved the use of the above colloidal silica material have demonstrated its highly chemical, reactive nature due to its fine particle size. Its wide distribution and adherent qualities give high surface area when dried, affording maximum possibility for chemical reaction to form silicates of an admixed refractory oxide during the annealing processing.

In addition to the above-described colloidal silica, the present coating composition preferably contains one or more finely divided refractory materials such as magnesia, lime, alumina, calcined dolomite, and zirconia, or mixtures of these refractory oxides.

In preparing the coating composition for application to the metallic sheets, a slurry is made from a dispersion of the colloidal silica and refractory oxide in water. In such a slurry it has been found that a colloidal silica content of from 1.5-6% by weight is effective, but it is to be understood that the invention is not necessarily limited to this range since various factors such as the desired viscosity and manner of applying the slurry may dictate the use of greater or lesser proportions of the colloidal silica. A range of refractory oxide content which has proved effective is from 2-7% by weight of the slurry. The maximum percentage of the refractory oxide will depend somewhat on the ease with which it can be maintained in the dispersed or suspended form in the slurry and the maximum thickness of the final coating which can be tolerated.

It has been found, however, that the ratio of refractory oxide (e. g. magnesium oxide) to colloidal silica is quite important, the preferred range of ratios of magnesium oxide to colloidal silica being from 1:1 to 8:1 by weight.

A typical coating composition found suitable as a separator insulation for 1000° C. hydrogen annealing of the magnetic steel strip has a magnesium oxide to colloidal silica ratio of 1:1 by weight, the water slurry composition being, in percent by weight, 6% MgO, 6% colloidal silica, and the balance water.

Another composition more suitable for 1175° C. and higher annealing temperatures has a magnesium oxide to colloidal silica ratio of 4:1 by weight, the water slurry composition being, in percent by weight, 6% MgO, 1½% colloidal silica, and the balance water.

The slurry may be applied in the form of a thin coating on the magnetic sheet material by any suitable means, such as by immersion, brushing, or spraying. The wet coating thus applied is dried by any suitable means, and if desired the drying process may be accelerated by heat-

ing at elevated temperatures. In this respect, the present coating composition has a distinct advantage over the prior coating materials which contained an organic binder such as the methyl cellulose mentioned above. At drying temperatures over 150° C. such organic materials decompose and become useless as binders, and as a result the coating is easily brushed from the surface of the metal after the annealing. To avoid this effect, it was necessary to unduly retard the process of drying coating compositions containing organic binders, a problem which has been overcome by the present composition.

After the coating has dried on the surface of the magnetic sheet material, the coated metal in either wound or stacked condition is placed in a furnace for box annealing, the coated material being annealed at temperatures up to 1200° C., but usually in the range of 700° to 1175° C. depending upon the particular magnetic material being treated.

During the annealing process the coating serves to separate the adjacent metal surfaces to prevent the metal sheets from sticking together. At the same time, the minutely subdivided colloidal silica reacts chemically with the magnesia (or other refractory oxide present), and this reaction coupled with the intimate contact which the colloidal silica has with the metal surface, forms a permanent tightly adherent insulating film of the refractory material on the metal surface. Such a film has been found to be produced on all of the various types of magnetic sheet materials. In some cases, as with silicon steel, this bonding may also be of a chemical nature resulting from the reaction of magnesia or other refractory oxide present with the constituents, such as silica, of the metal.

The thin refractory coating thus formed may have a thickness of about 0.1 mil or less, and has excellent insulating properties effective to electrically insulate the metal laminations or windings from one another during subsequent use in a transformer core, motor armature, or the like.

To determine the insulating characteristics of a typical coating made in accordance with the invention, a coating of the colloidal silica and magnesia was prepared and applied as described above on silicon steel laminations, which were thereafter annealed at 1000° C. in pure, dry hydrogen. After anneal, the surface insulation characteristics of the resulting refractory film were determined by the Franklin test, in which readings of one ampere represent no surface insulation and zero amperes represent perfect insulation. For good transformer usage, it is desirable that the Franklin reading be less than 0.20 ampere. The average Franklin reading of various samples of the silicon steel coated in accordance with the invention was .13 amperes, showing entirely satisfactory insulating qualities.

The coatings of the present invention have several advantages over those previously employed. As mentioned, the drying period may be considerably shortened. Further, by dispensing with the use of binder substances, the separator coatings may be made thinner than heretofore and hence provide a space factor advantage during the annealing operation. In addition, the minute nature of the colloidal silica makes possible a more intimate bond with the metal surface as well as a greater bonding reaction between the materials to be joined, thereby providing a more tightly adherent and uniform layer of superior insulating properties.

In this connection it is to be emphasized that it is due largely to the unique nature of the particular type of colloidal silica used, as described above, that the improved insulating coating is made possible, and it is to be understood that the expression "colloidal silica" as used in the claims is intended to mean a colloidal silica having the properties described in detail above. It is also intended to include in the expression "sheet material" as used in the claims forms such as strips, tapes, and other laminar shapes.

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What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A metallic sheet material having thereon a thin tightly adherent coating composed of a finely divided inorganic refractory material formed by application of a slurry consisting essentially of an aqueous solution containing  $\text{SiO}_2$  in the form of reactive, submicroscopic particles and at least one refractory oxide, said inorganic refractory material during anneal of the metallic sheet material forming a permanent, electrically insulating layer firmly bonded to the surface of the metallic sheet material.

2. A magnetic sheet material having thereon a thin tightly adherent coating composed of a finely divided inorganic refractory material formed by application of a slurry consisting essentially of an aqueous solution containing  $\text{SiO}_2$  in the form of reactive, submicroscopic particles and magnesia, said inorganic refractory material during anneal of the magnetic sheet material forming a permanent, electrically insulating layer firmly bonded to the surface of the magnetic sheet material.

3. A silicon steel sheet material having thereon a thin tightly adherent coating composed of a finely divided inorganic refractory material consisting essentially of colloidal silica composed of reactive, submicroscopic particles of the order of 10-30 millimicrons in size and at least one refractory oxide, said inorganic refractory material during anneal of the silicon steel sheet material forming a permanent, electrically insulating layer firmly bonded to the surface of the silicon steel sheet material.

4. The method of providing a separating and electrically insulating coating for metallic sheet material which comprises applying to the surface of the metallic sheet material a suspension of a finely divided inorganic refractory material consisting essentially of an aqueous solution containing  $\text{SiO}_2$  in the form of reactive, submicroscopic particles and at least one refractory oxide; drying the thus applied suspension so as to form a refractory coating on the surface of the metallic sheet material; and annealing the thus coated sheet material in multi-ply assembly with the refractory coating separating adjacent surfaces of said sheet material, so as to form a permanent, tightly adherent, electrically insulating layer of refractory material on the surface of the metallic surface material.

5. The method of providing a separating and electrically insulating coating for magnetic sheet material which comprises applying to the surface of the magnetic sheet material an aqueous suspension of a finely divided in-

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organic refractory material consisting essentially of colloidal silica composed of reactive, submicroscopic particles of the order of 10-30 millimicrons in size and at least one refractory oxide; drying the thus applied aqueous suspension so as to form a refractory coating on the surface of the magnetic sheet material; and annealing the thus coated sheet material in multi-ply assembly with the refractory coating separating adjacent surfaces of said sheet material, so as to form a permanent, tightly adherent, electrically insulating layer of refractory material on the surface of the magnetic surface material.

6. The method of providing an insulating coating for metallic sheet material which comprises applying to the surface of the metallic sheet material an aqueous suspension of colloidal silica composed of reactive, submicroscopic particles of the order of 10-30 millimicrons in size and at least one refractory oxide, the ratio of colloidal silica to the refractory oxide being from 1:1 to 1:8 by weight; and heating the thus applied suspension at a temperature of from  $700^\circ$ - $1200^\circ$  C., to thereby form a permanent, tightly adherent, electrically insulating layer of refractory material on the surface of the metallic sheet material.

7. The method of providing an insulating coating for magnetic sheet material which comprises applying to the surface of the magnetic sheet material an aqueous suspension of colloidal silica composed of reactive, submicroscopic particles of the order of 10-30 millimicrons in size and magnesium oxide, the ratio of colloidal silica to the magnesium oxide being from 1:1 to 1:8 by weight; drying the thus applied aqueous suspension so as to form a refractory coating on the surface of the magnetic sheet material; and annealing the thus coated sheet material in multi-ply assembly at a temperature of from  $700^\circ$ - $1200^\circ$  C. with the refractory coating separating adjacent surfaces of said sheet material to thereby form a permanent, tightly adherent, electrically insulating layer of refractory material on the surface of the magnetic sheet material.

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