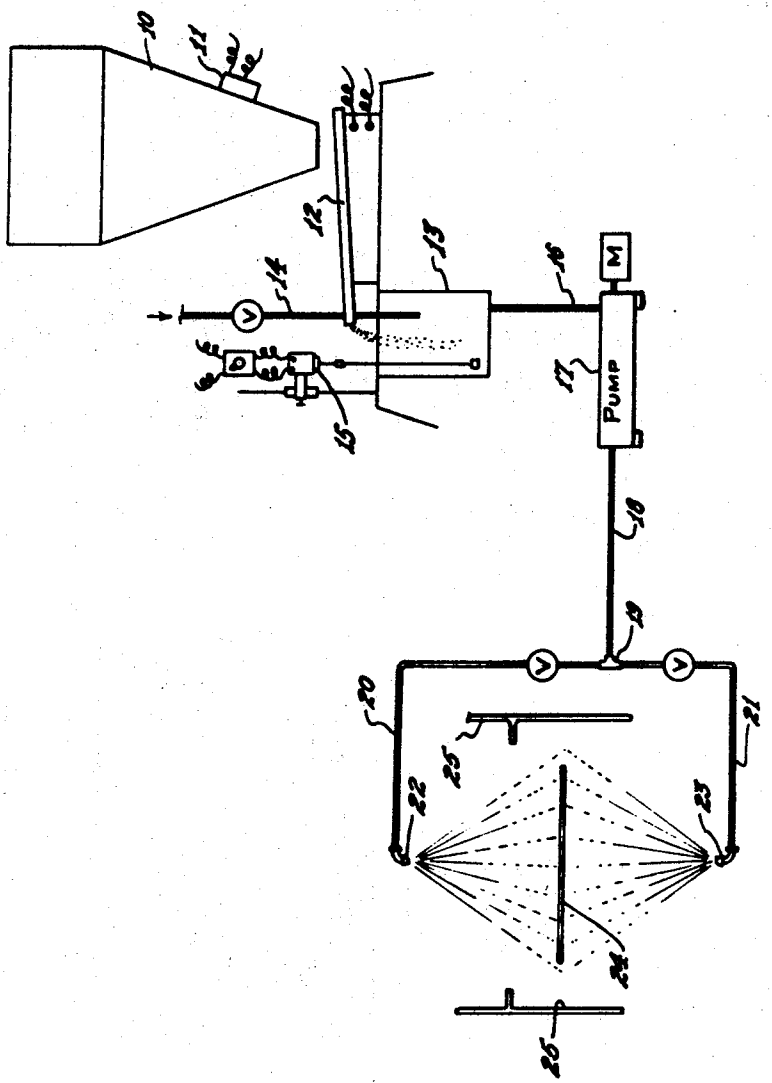
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PRODUCTION OF INSULATIVE COATINGS ON SILICON STEEL STRIP

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PRODUCTION OF INSULATIVE COATINGS ON SILICON STEEL STRIP

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This invention relates to the application of refractory annealing separators and especially those resulting in the production of insulative coatings on silicon steel strip. The production of glassy coatings on silicon steel surfaces has been taught in the Carpenter et al. patent, No. 2,385,332 of September 25, 1945, the Carpenter et al. patent, No. 2,492,682 of December 27, 1949, and the Carpenter patent, No. 2,533,351 of December 12, 1950. This application is a continuation-in-part of our copending application, Serial No. 402,994, filed January 8, 1954, and now abandoned.

Such glass-like coatings confer upon stock, which is to be used for laminated cores of magnetic apparatus, a high surface resistivity while maintaining a high space factor. As taught in the above mentioned patents, the process involves preferentially oxidizing silicon in the sheet stock adjacent the surface thereof to form silica, coating the surface of the stock with a magnesia-bearing substance and heat treating the stock to cause the magnesia to combine with the surface silica to form a glass.

According to the first named Carpenter patent, the magnesia-bearing material applied to the sheet stock was milk of magnesia, i.e. hydrated magnesium oxide. According to the teachings of that patent, a thick creamy and adhesive suspension principally of magnesium hydroxide in water was applied to the strip prior to the high temperature box anneal.

According to the second named patent, the sheet stock was coated with a slurry of magnesium or calcium hydroxide and the free water was driven off by gentle heat and the sheets were then passed into a continuous annealing furnace in which the hydroxide was converted to the oxide and surface silicon converted to silica, which formed glass with the alkaline earth oxide during a subsequent high temperature anneal.

According to the third of the patents named above, the sheets were coated on both sides with magnesia-bearing material, preferably magnesium hydroxide, and then passed into a furnace containing a wet hydrogen atmosphere where the glass-forming process was carried to completion without a subsequent box anneal.

There have been some objections to all of the methods of getting the magnesia-bearing material onto a sheet or strip stock. Where the magnesia has been put on in the form of magnesium hydroxide which was calcined in the high temperature box annealing step, the serious objection was encountered that the large quantity of water of hydration given off during the heatup required special measures to prevent it from oxidizing the steel. This oxidation frequently causes the silicon steel to be excessively brittle for punching, slitting, and core winding operations, especially in the material annealed in coil form. Some attempt to avoid trouble from this source involved the provision of unusually large atmosphere drying equipment. Other costly measures have also been taken.

The same problems have been encountered when other

alkaline earth oxides, such as calcium oxide, were applied as annealing separators to prevent coil turns or adjacent sheets from sticking together, whether or not conditions were maintained to cause the formation of an insulative glass coating.

In describing our invention we shall refer throughout to magnesia (MgO) as an example of the type of annealing separator with which our invention is concerned. We wish it to be understood, however, that our invention applies equally to lime (CaO), to other alkaline earth oxides, and to mixtures containing any of them in effective amounts.

In an effort to overcome this difficulty from water of hydration, attempts have been made to apply magnesia in the form of a dry powder thoroughly calcined. When this is attempted with strip stock, it has been found that the magnesia powder will not stay on the surface of the strip during the coiling operation but will actually be blown out from between the laps of the coils.

It has also been attempted to mix magnesia with an organic vehicle having a low boiling point and being anhydrous, such as naphtha or carbon tetrachloride. These attempts have been proven impractical because of the danger of fire or explosion and the toxic effects of the fumes and also because of the tremendous expense entailed in setting up a suitable recovery system for the organic vehicle.

With the foregoing considerations in mind, it is the principal object of our present invention to provide a method of applying the necessary alkaline earth oxide annealing separator to the strip while avoiding all of the bad effects discussed above. It is another object of our invention to provide a method of applying the alkaline earth oxide in such a way as not to recarburize the steel and also so as not to oxidize the steel excessively. It is still another object of our invention to provide a method as outlined above which will be extremely simple and quite inexpensive so as not to increase the production cost of the glass coated silicon steel.

These and other objects of our invention which we shall point out in more detail hereinafter or which will be apparent to one skilled in the art upon reading these specifications, we accomplish by that series of method steps of which we shall now disclose exemplary embodiments.

Reference is made to the single drawing showing diagrammatically an apparatus for carrying out our method.

Briefly, in the practice of our invention we make use of a particular grade of magnesia with regard to the physical properties thereof and we mix the magnesia with water and apply it to the strip very rapidly and immediately dry the strip to volatilize the uncombined water so as to achieve on the strip a coating of magnesia with a hitherto unobtainable minimum of combined water. As far as the magnesia is concerned, the principal physical properties which we consider important are the hydration rate, the particle size and the carbon dioxide content.

To achieve the maximum benefits of our invention, the magnesia should be of a type which hydrates very slowly. It is well known that, depending on the conditions under which magnesia has been calcined, it will hydrate more or less rapidly. In general, magnesia which has been calcined at high temperatures will hydrate much more slowly than magnesia which has been calcined at relatively low temperatures. We have found that a calcining temperature of 1040° C. is sufficiently high under most conditions to yield a magnesia which will hydrate sufficiently slowly to achieve our result. This calcining temperature is not alone the criterion of the suitable rate of hydration, as it also is dependent on other variables

such as the nature of the raw material, the time held at calcining temperature, and the particle size. These variables can be adjusted in manners well known in the calcining art and form no part of our invention. Magnesia, having a low hydration of not more than 12% of combined water when applied in accordance with the teachings of this application, can be purchased on the market, as it is used as an ingredient in heat refractories.

In order to determine the suitability of a magnesia for our purposes, we have developed a simple test for its hydrating capacity. A sample of magnesia to be tested is mixed with water at 65° F. in the proportion of about 1 part by weight of magnesia to about 8 parts by weight of water (approximately 1 pound MgO to 1 gallon water). The resulting slurry is spread upon a sheet of steel and dried in an oven at about 400° F. to drive off the free water. The magnesia is then scraped off the sheet and analyzed for total water content after the magnesia has been in contact with the water for periods of 1 minute, 3 minutes and 10 minutes. If the water content is at no time above 12%, and if the water content does not appreciably increase between 1, 3 and 10 minute tests (within the accuracy of the test) the magnesia is satisfactory for our purposes.

It should be borne in mind that according to our present invention, the water is intended to serve merely as a vehicle for getting the magnesia onto the strip. It is our aim to get the magnesia onto the strip and drive off the free water before there has been any substantial degree of hydration. In the apparatus which we use, and it will be described briefly hereinafter, the magnesia is contacted with water and intimately and rapidly mixed and pumped through spray nozzles onto the strip immediately before the strip enters a drying furnace. The strip moves at a speed of from 80 to 140 feet per minute and the drying oven is perhaps 20 feet long, so that the length of time from initial contact of the magnesia and water to the time when all the free water has been driven off when the strip emerges from the furnace is not more than two or three minutes. It is our object to have a minimum of combined water, and in any event not more than 12% combined water in the magnesia coating when the strip emerges from the furnace.

A very important characteristic of the magnesia which we use is particle size. We consider that particle size is important because it has an effect on the hydration rate and because a proper particle size will prevent telescoping of the coil on the coiling apparatus.

The particle size of the magnesia is not very critical as long as the very finest grades which hydrate more rapidly are avoided. It can be reasonably fine so as to spread on the sheet readily, and we have had excellent results with a magnesia in which the weight median particle size ranges from 5 to 15 microns. The weight median particle size may be defined as the dividing size between two groups of equal weight, one containing all particles larger than the weight median size, and the other containing all particles smaller than the weight median size. If the coated stock is to be coiled, we have found that very large particle sizes should be avoided, as they will tend to make the coil turns slide on one another and the coil may telescope. To avoid this, we prefer to keep the particle size small enough that 98% will pass through a 325 mesh screen. This means that the bulk of the particles is not greater than 44 microns in size.

Since the steel which is being treated by our invention has been decarburized down to a carbon content of about .005%, it is important not to recarburize the steel. Magnesia commonly contains CO_2 and according to our teachings the CO_2 content must be low enough so that no substantial recarburization can take place. We have found that with a magnesia containing as much as 6% CO_2 objectionable carburizing effects can take place. We consider that excellent results are obtained with a CO_2 content below 2% although for some purposes a CO_2 content greater than 2% but less than 6% can be tolerated.

According to our invention, we mix the finely divided calcined magnesia with water to provide a slurry of uniform consistency for application to the strip. Since the hydration rate increases with an increase in temperature and since we require a minimum of hydration, we prefer to use water not substantially warmer than room temperature or even refrigerated water. We have obtained successful results where the water was at a temperature of about 20° C. in commercial operation and have successfully used temperatures up to 30° C. with very low hydrating capacity magnesia (less than 2% water), and following the other teachings of this invention.

We have found that a proportion of 1 pound of magnesia per gallon of water makes a slurry of suitable consistency for use in our apparatus. This proportion is not highly critical and can be varied depending upon the nature of the pumping apparatus, the type of nozzle and the squeegeeing arrangement which is used.

In the mixing of the magnesia or magnesia-bearing material and water, the length of time that the water and magnesia are in contact and the violence with which they are mixed are important and these factors are related. The more horse power applied in the mixing operation, the shorter the time of contact may be. We desire to produce completely intimate contact of the water and magnesia as rapidly as possible and to minimize the length of time in contact. In actual practice with the apparatus shown in the drawing, the length of time from initial contact of the magnesia and water and the spraying of the slurry onto the strip is about two minutes and the length of time before the strip has passed through the drying furnace and the water has been driven off is less than a minute, i.e. a matter of seconds.

The slurry may be applied to the strip in many ways but we prefer to spray it onto both sides of the strip simultaneously, and then to squeegee it by means of squeegee rolls to insure complete spread and to control the thickness of the coating.

We have made tests to determine the amount of hydration obtained by mixing a weighed amount of magnesia with a measured amount of water, the water being of a temperature of 20° C. for about two minutes and have then applied the slurry to a test sheet which we then dried at a temperature below calcining temperature. We then scrape the magnesia off the test sheet and determine the water content. We have found that if we have selected the proper grade of magnesia and have otherwise followed the teachings of our invention we achieve a combined water content of not more than 12% of the weight weight of the magnesia coating.

We prefer a coating containing not more than 2% of combined water and with this coating weights of magnesia as high as .1 ounce per square foot of sheet have been applied with optimum results. When thinner coatings are used, say down to about .03 to .04 ounce, combined water contents of about 5 to 8% have been used with nearly as good results. Heavier coatings containing as much as 12% water can be used with results superior to conventional methods if other teachings of the invention are followed.

In the drawing, we have indicated at **10** a hopper into which the magnesia is fed. The hopper is agitated by an electromagnetic vibrator **11** so that the magnesia is continuously and slowly fed onto a vibratory feeder **12**. The magnesia slowly feeds off the end of the vibratory feeder **12** into the mixing tank **13**. Water is added at a controlled rate through the line **14**. The water and magnesia are mixed by means of a conventional mixing device **15**. The slurry passes out through a line **16** to a motor driven pump **17** and through a line **18** to a T-fitting **19**. From here the slurry passes from the lines **20** and **21** to the nozzles **22** and **23** by which it is sprayed onto both

sides of the strip 24 simultaneously. Splash shields are preferably provided at 25.

Since the invention may be applied to steel sheets as well as to steel strip, the term strip as used in the claims is to be understood as not necessarily defining a great length of material, but as inclusive of sheet stock and strip stock, as these words are understood in the steel industry.

It will be clear that numerous modifications may be made without departing from the spirit of the invention and we, therefore, do not intend to limit ourselves except as set forth in the claims which follow.

Having now fully described our invention, what we claim as new and desire to secure by Letters Patent is:

1. In the process of producing refractory annealing coatings on the surface of steel strip, the steps of: mixing an alkaline earth oxide with water, said alkaline earth oxide being in finely divided form and containing less than 6% by weight carbon dioxide and having a very low hydration rate, said water being at a temperature of about 20° C. (not substantially higher than 30° C.), the mixing of said alkaline earth oxide and said water being such as to produce completely intimate contact of said oxide and said water as rapidly as possible so as to minimize the length of time said oxide and said water are in contact and so as to provide a slurry of uniform consistency for application to the strip; applying the alkaline earth oxide-water slurry to the strip to coat the same uniformly; and drying the strip as rapidly as possible to drive off the free water; said steps of mixing, applying and drying being carried out sufficiently rapidly to produce, on the strip, a coating having not more than 12% combined water.

2. The process of claim 1, wherein the alkaline earth oxide contains not more than 2% by weight of carbon dioxide.

3. The process of claim 1, wherein the particle size of the alkaline earth oxide is such that 98% of the particles will pass through a 325 mesh screen.

4. The process of claim 1, wherein the bulk of the particles of the alkaline earth oxide is not greater than 44 microns in size.

5. The process of claim 1, wherein the weight median particle size of the alkaline earth oxide is from 5 to 15 microns.

6. The process of claim 1 in which the slurry is applied by being sprayed onto both sides of the strip simultaneously and squeegeeing the strip on both sides to insure uniform distribution and to control the thickness of the coating.

7. The process of claim 1, wherein approximately 1 pound of the alkaline earth oxide is used per gallon of water.

8. The process of claim 1 in which said alkaline earth oxide has a weight median particle size of from 5 to microns and contains not more than 2% by weight of carbon dioxide, and in which the proportions in mixing are about 1 pound of said alkaline earth oxide per gallon of said water.

9. The process of claim 1 in which said alkaline earth oxide is a magnesia bearing oxide and in which the step of drying is accomplished by heating.

10. The process of claim 9 in which said magnesia bearing oxide has a weight median particle size of from 5 to 15 microns and contains not more than 2% by weight of carbon dioxide, and in which the proportions in mixing are about 1 pound of said magnesia bearing oxide per gallon of said water.

11. The process of claim 9, wherein the magnesia contains not more than 2% by weight of carbon dioxide.

12. The process of claim 9, wherein the particle size of the magnesia is such that 98% of the particles will pass through a 325 mesh screen.

13. The process of claim 9, wherein the bulk of the particles of the magnesia is not greater than 44 microns in size.

14. The process of claim 9, wherein the weight median particle size of the magnesia is from 5 to 15 microns.

15. The process of claim 9 in which the slurry is applied by being sprayed onto both sides of the strip simultaneously and squeegeeing the strip on both sides to insure uniform distribution and to control the thickness of the coating.

16. The process of claim 9, wherein approximately 1 pound of the magnesia is used per gallon of water.

References Cited in the file of this patent

UNITED STATES PATENTS

2,385,332	Carpenter et al.	Sept. 25, 1945
2,533,351	Carpenter	Dec. 12, 1950
2,739,085	McBride	Mar. 20, 1956

OTHER REFERENCES

Meller's Modern Inorganic Chemistry, revised edition, 1939, page 222.