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Oct. 15, 1946. A. R. McGARVEY 2,409,297

PROCESS FOR PRODUCING MOLDED BASIC MAGNESIUM CARBONATE

Filed May 1, 1942 3 Sheets-Sheet 1

Col 11

Fig. 1

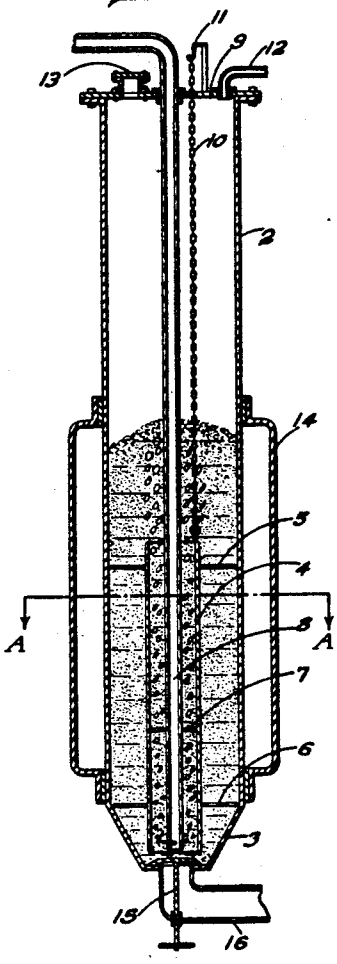


Fig. 3

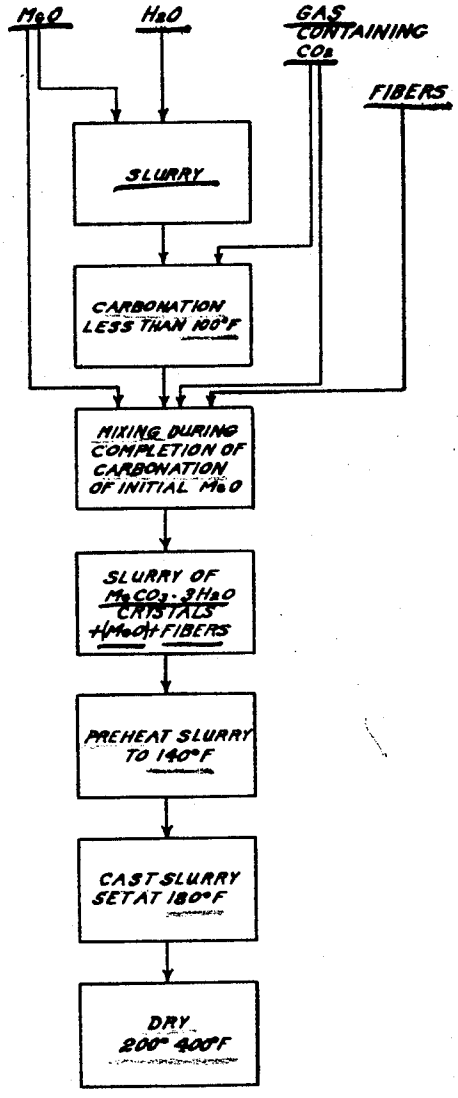
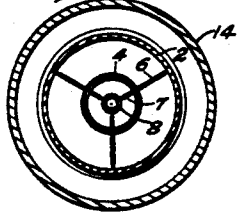


Fig. 2

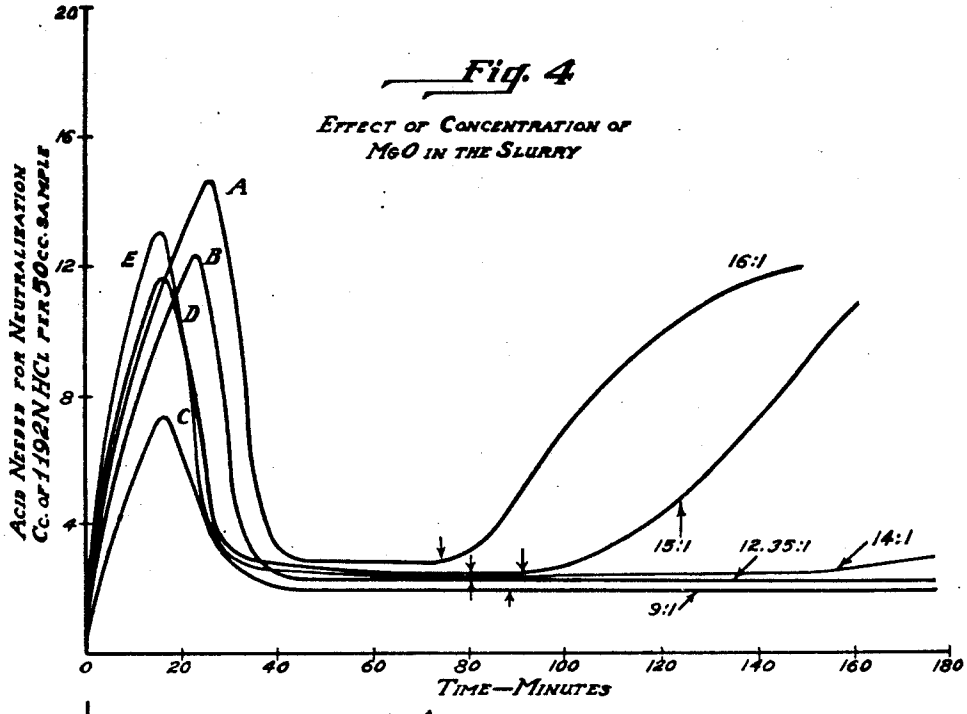


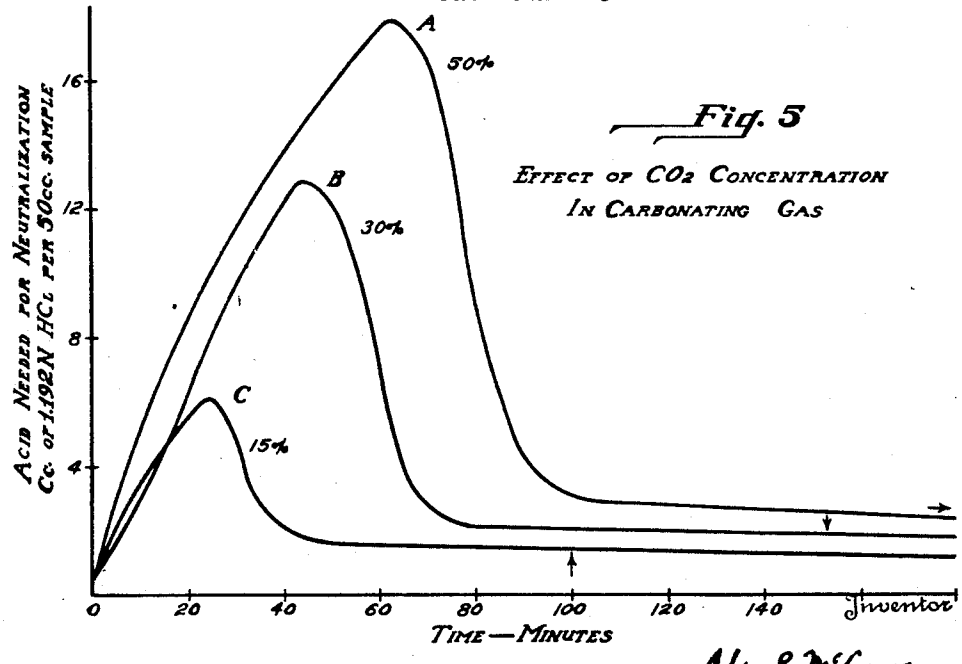
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PROCESS FOR PRODUCING MOLDED BASIC MAGNESIUM CARBONATE

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PROCESS FOR PRODUCING MOLDED BASIC MAGNESIUM CARBONATE
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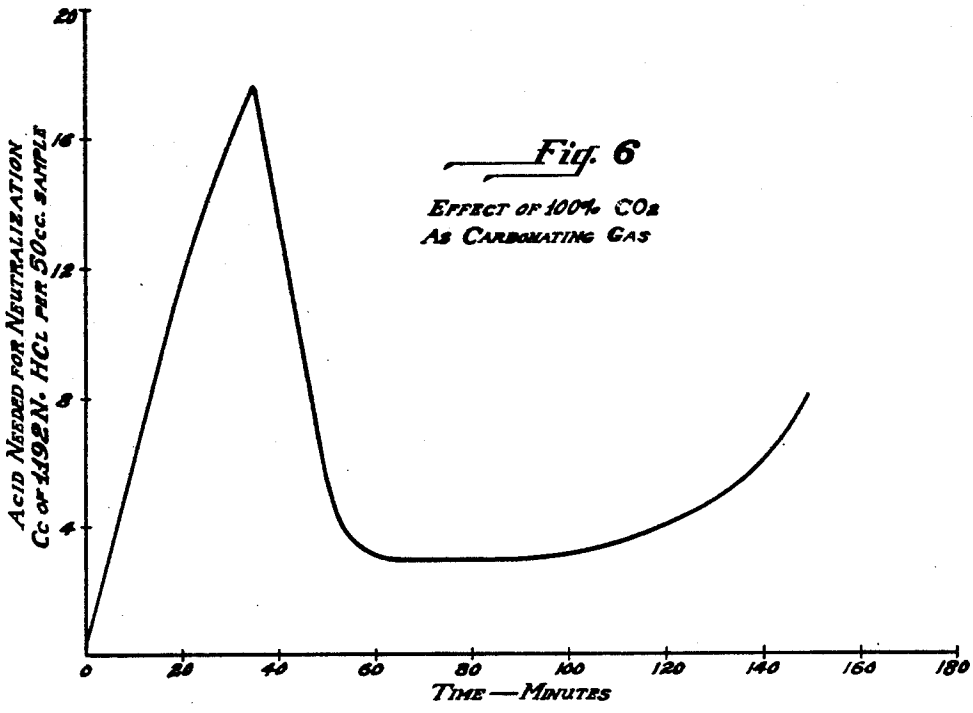


Fig. 6

EFFECT OF 100% CO_2 AS CARBONATING GAS

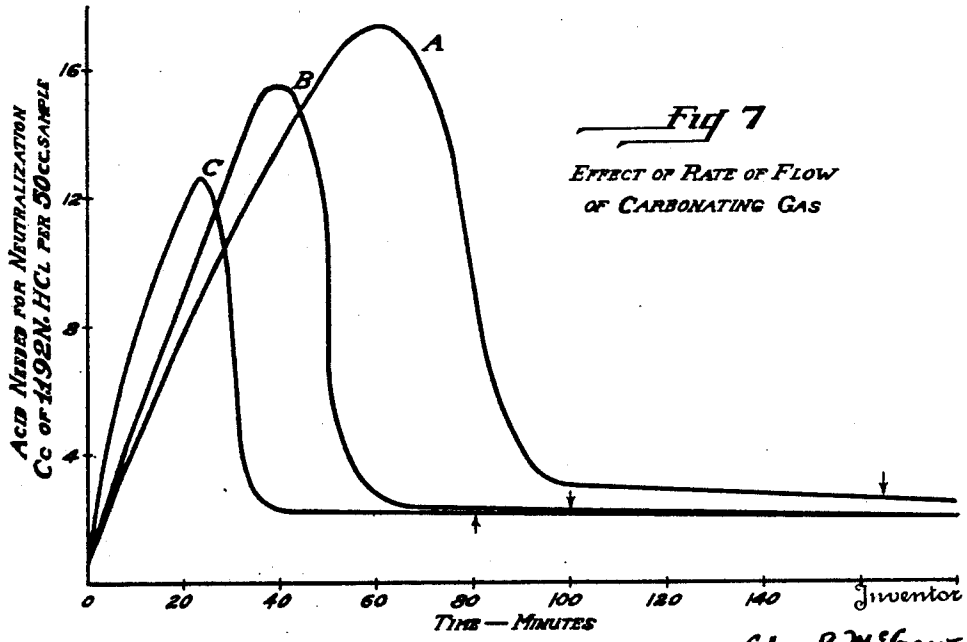


Fig 7

EFFECT OF RATE OF FLOW OF CARBONATING GAS

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UNITED STATES PATENT OFFICE

2,409,297

PROCESS FOR PRODUCING MOLDED BASIC MAGNESIUM CARBONATE

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Application May 1, 1942, Serial No. 441,380

12 Claims. (Cl. 106—121)

work etc. here
See Col 11

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This invention relates to the production of light basic magnesium carbonate, and especially that commonly known as "85% magnesia."

This application is a continuation-in-part of my copending application, Serial No. 385,612, filed March 28, 1941.

This invention is concerned with an improved method of making a product of this class having markedly improved strength and hardness and not exhibiting the excessive weakness, brittleness, and fragility of the products heretofore produced by such of the known processes as employ a comparable procedure. The type of process with which the invention is primarily concerned is that in which an aqueous suspension of magnesium hydroxide or magnesium oxide is converted by a simple direct process, without the necessity of removing water, into an aqueous slurry of such a constitution that the entire slurry sets to a form of basic magnesium carbonate which is self-sustaining and can be dried without shrinking to a form having predetermined density, fixed by the amount of water in the initial suspension, and having the shape of the mold in which it has set. The success of the procedure employed according to the invention depends upon proper control of conditions surrounding the reaction, primarily during the step of carbonation, and the treatment of the slurry prior to the step of molding.

One process of this type previously employed involved the carbonation of a dilute aqueous suspension of magnesium oxide to form the carbonate, mixing asbestos in the resulting carbonated suspension, shaping the mixture, converting the product to basic carbonate, and drying the product. Such processes purposely employed greatly diluted slurries of magnesium oxide. A slurry containing an amount of water ranging from fifteen to twenty-five (and even as high as sixty) times the amount of magnesium oxide by weight is representative of the dilutions suggested and commonly employed, and such dilution was thought necessary to avoid difficulties in controlling economically and practically the reaction conditions in order to produce a carbonate having self-setting properties. Products resulting from this procedure, in which the steps of removing water and then reconstituting a slurry of the self-setting reaction product were omitted, while of light weight and of high insulating value, were excessively weak, brittle and fragile. The products were so lacking in structural strength that a mere handling of them, no matter how careful, frequently resulted in serious

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deformity and breakage. It was a common occurrence for blocks even of as small a size as 15" x 4" x 1½" to bear indentations corresponding to the fingers of persons who had previously picked them up in the normal processes of packing, shipping, and erecting the material.

The previously employed processes of making the self-setting magnesium carbonate by carbonating a slurry of magnesium oxide or hydroxide had to be carefully controlled to avoid the formation of detrimental amounts of magnesium bicarbonate by excessive carbonation. The presence of substantial amounts of this soluble magnesium salt retards setting of the self-setting product, gives rise to gas pockets and fissures, and impairs the strength of the final block. Because of the difficulty of avoiding the formation of this soluble salt, it has previously been preferred to permit it to form and then remove it. Therefore, the general practice has been to remove by filtration or decantation a large amount of the water (and thereby rid the product of the soluble bicarbonate of magnesium) after the carbonation has been performed and to thereafter reconstitute a suspension of the self-setting crystalline product by agitating it in a fresh supply of a lesser amount of water; alternatively, the reaction product resulting from the carbonation has been allowed to settle, and so much of the water overlying the sediment has been removed that the sediment can be resuspended by agitation in the lesser amount of water, after which the product has been poured into forms and has been allowed to set. The products resulting from this procedure are of correspondingly greater density and of greater strength than those obtained from the type of process in which the original slurry containing the proportionately larger amount of water was, after carbonation and mixing in the fibers, poured directly into the mold for setting. However, in this procedure, the necessity of agitating the crystals to prepare the final slurry for setting prevents the achievement of the maximum possible internal structural strength in combination with the minimum possible density which is, of course, the ultimate desideratum in the manufacture of insulating materials. As explained more fully hereinafter, this agitation results in a weakened bond and increased density in the molded products.

In order to overcome the inherent disadvantages of weakness, brittleness, and fragility of the products resulting from the direct process in which no water is removed, Williams, in accordance with the disclosure of Patent 2,172,861, adds

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a water-soluble soap to the composition which is intimately mixed into the slurry of self-setting reaction product by agitation performed mechanically or by the bubbling of a gas through the slurry. However, it is desirable to avoid the inherent disadvantage resulting from the incorporation of a water-soluble material, such as soap, which renders the final product too easily affected by conditions of relatively high humidity.

I have now found that by a proper control of conditions, products having increased hardness and strength for a given density can be made by a simple direct process without subsequent removal of water before molding the product. It has also been found possible to control the process so that no bicarbonate of magnesium is formed even after excessive carbonation. The materials resulting from my improved process do not exhibit the brittleness and fragility inherent in such as have been heretofore produced by generally similar processes, and there is no necessity of employing materials of an essentially foreign character to impart the requisite qualities desired in the product.

In the drawings,

Figure 1 is an elevational cross-section view of a carbonator;

Figure 2 is a sectional view taken on line A—A of Figure 1;

Figure 3 is a flow sheet illustrating one embodiment of my process;

Figure 4 is a graph showing the effect of concentration of the magnesium oxide in the slurry;

Figure 5 is a graph showing the effect of the carbon dioxide concentration in the carbonating gas;

Figure 6 is a graph showing the effect of 100% carbon dioxide as the carbonating gas; and

Figure 7 is a graph showing the effect of the rate of flow of the carbonating gas through the slurry.

In accordance with my invention, I have found that carbonation of a relatively concentrated slurry of the magnesium oxide or magnesium hydroxide can be effected with the production of either a tabular plate-like or a fine needle-like crystalline form of normal magnesium carbonate having self-setting properties by properly controlling the conditions of carbonation so that the temperature within the reacting mass remains as close to room temperature as possible and in no case attains a temperature above about 100° F. and preferably remains at least as low as 75° F. to 85° F.

I have found, surprisingly, that substantially no magnesium bicarbonate is formed no matter how excessive the carbonation when slurries having a dilution ranging from about nine parts up to about fourteen parts by weight of water to one part by weight of magnesium oxide are treated with dilute carbon dioxide gas, whereas when greater dilutions are employed magnesium bicarbonate is formed immediately upon the occurrence of excessive carbonation and increases in amount steadily upon continuation of such excessive carbonation. By excessive carbonation is meant the continued introduction of carbon dioxide into the slurry after tests show that the slurry contains dissolved therein only so much magnesium as corresponds to the solubility of the normal magnesium carbonate under the operating conditions of temperature and pressure.

In Figure 4, curves A, B, C, D, and E show the amount of magnesium compounds dissolved in five differently concentrated slurries of magnesium oxide at any particular time during the carbonation. The amount of dissolved magnesium compounds was measured by the amount of hydrochloric acid needed for neutralization of 50 cc. of the filtered slurry, using methyl orange as an indicator. The ratio of the water to magnesium oxide for each of the curves was as follows:

Curve	Ratio H_2O:MgO
	Parts by weight
A	16 to 1
B	12.35 to 1
C	9 to 1
D	15 to 1
E	14 to 1

For carbonating, a gas mixture containing 50% of air and 50% of carbon dioxide by volume was used. The gas was introduced at the rate of about 35 cubic feet per hour per gallon of slurry.

All of the curves start from a common origin corresponding to the normal solubility of magnesium oxide in water at the temperature employed. The humps at the left of each of the curves show that magnesium bicarbonate in considerable quantities was produced early in the reaction. During this time no normal magnesium carbonate was formed until the peaks of the humps are reached, after which the crystals of normal carbonate were formed rapidly and the bicarbonate decreased in amount until it substantially disappeared when the reaction was complete. The magnesium oxide or hydroxide content initially present decreased continually until the reaction was complete. An arrow is placed upon each curve to indicate at what time the formation of the hydrated normal magnesium carbonate was completed for all practical purposes. The two opposed arrows indicate this point for curves B, and E, for the time at which the formation of the hydrated normal magnesium carbonate was completed was substantially the same. It should be noted, however, with respect to curves A and D, where dilute slurries of magnesium oxide having concentrations of 16:1 and 15:1 respectively were carbonated, that substantially at the time of completion of the reaction the formation of magnesium bicarbonate again started to take place, thereby necessitating either close control of the time of termination of the carbonation reaction or subsequent addition of magnesium oxide to neutralize the bicarbonate. Curves B, C, and E, however, show that such control or addition of magnesium oxide is not necessary when a more concentrated slurry having less than 15 parts of water to 1 part of magnesium oxide is employed in the carbonation.

In accordance with my invention, therefore, I employ the more concentrated magnesium oxide slurries specified above and preferably a dilution of from about 12 to 13 parts of water to 1 part of magnesium oxide. Thereby, the difficulties involved in avoiding excessive carbonation and the necessity to add alkaline materials to neutralize whatever bicarbonate is formed are eliminated in my process. Furthermore, the step of washing out the bicarbonate by removing the water from the slurry at the end of the carbonation and the consequent necessity to resuspend the mass of crystals in a fresh supply of water may be eliminated. While the procedure involving reconstituting the crystals in a fresh slurry may be employed, for reasons explained more fully hereinafter such

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a procedure is preferably avoided, since the elimination of the agitation needed to resuspend the crystals results in the production of stronger and harder final blocks having correspondingly lighter densities and higher insulating capability.

The concentration of the slurries may be greater or lesser than 12 to 13 parts of water to 1 part of magnesium oxide, for example a concentration of 10:1 or 14:1 may be employed. However, as the slurries become more concentrated a material having a relatively high density is obtained. When a concentration greater than one part of magnesium oxide to 9 parts of water is reached, the material obtained is too dense to be commercially practical. On the other hand, when less concentrated slurries are utilized the materials obtained tend to become lighter and more fragile. When a concentration of, or less than, one part magnesium oxide to 15 parts of water is utilized, the bicarbonate is formed in excessive amounts causing fissures and gas pockets in the final product. MgO can be added to neutralize the bicarbonate, but such a procedure results in the production of a softer block than is desirable.

The preferred procedure therefore involves the elimination of the step of removing the water present during the carbonation and that of resuspending the crystals in fresh water. By proceeding in this manner, it is possible to predetermine the final density of the molded insulating material by controlling the amount of water used at the start of the carbonation; the more water used, the lighter the final molded material. However, in those cases in which these two steps are not eliminated, the final density of the block can be controlled by adjusting the amount of water in the step of resuspending the crystals.

I have also found that by employing the more concentrated slurries specified above, the formation of sheaves of crystals which occurs generally with the greater dilutions of the prior art is substantially eliminated. The presence of a large number of sheaves results in a denser block of weaker structure.

When the prevailing temperature throughout the carbonation does not exceed 50° F., the tabular or plate-like crystals predominate in the product, while if a temperature of about and not in excess of 70° F. prevails, the crystalline product comprises about 50% of the tabular crystals and about 50% of the needle-like crystals. At temperatures of about 74° F. or higher, no tabular crystals are produced. For the purposes of this invention, it is considered immaterial whether the tabular or the needle-like variety of crystal is formed in the process of carbonation, since it has been found that, even in those processes starting with the tabular form of crystal alone or in admixture with the needle-like variety, the tabular crystals are gradually converted into the needle-like crystals at temperatures above about 70° F., this conversion occurring with great rapidity at about 123° F. Such conversion occurs in the step during which the slurry of the crystals is heated to cause setting as will be more particularly described hereinafter. For the same reason, the crystals formed in the carbonation process of this invention will be hereinafter referred to as "self-setting crystals" whether they are actually the tabular or the needle-like variety or a mixture of both since both varieties in effect set in the same manner.

However, in all cases it is highly important that the carbonation temperature be prevented from exceeding about 100° F. since it has been found

that in the process of this invention, wherein the crystals are formed directly by carbonation of magnesium oxide or hydroxide (without the intervening step of converting all the magnesium into the form of a soluble bicarbonate and then precipitating the self-setting crystals by heating the solution in accordance with a process heretofore employed) the self-setting crystals are partially converted to the form of a basic magnesium carbonate to an appreciable extent at temperatures above about 100° F., apparently because of the fact that the self-setting crystals are formed in the presence of magnesium oxide or hydroxide. This is unexpected in view of the fact that it has been found that no appreciable change to basic carbonate occurs when self-setting crystals are produced in processes involving the heating of magnesium bicarbonate until the temperature approximates 155° F. It should be noted at this point that the crystals formed in accordance with the process of this invention are much finer in size than such as are produced by heating magnesium bicarbonate solutions, the finer size imparting a greater strength to the final product.

The tabular crystals as well as the needle-like variety, the latter being probably in the rhombic crystallographic class, though some authorities place them in the hexagonal class, can be filtered and dried by acetone at low temperatures without any conversion to a basic carbonate form. Such dried crystals can be stored indefinitely in a dry atmosphere and can then be suspended in water and the suspension will set in the same manner as the carbonated slurries as hereinafter described. The tabular or plate-like crystals formed at low temperatures are probably the pentahydrate of the constitution $MgCO_3.5H_2O$. It is believed that the needle-like self-setting crystals have a composition corresponding to the formula $MgCO_3.3H_2O$. However, there is some authority holding that the composition of the needle-like crystals corresponds to the formula $Mg(OH).HCO_3.2H_2O$. Whatever the formula, it is known that such crystals while in the wet condition set slowly and are converted even in the cold to a form of magnesium carbonate entirely lacking the self-setting characteristics of the initially obtained crystals, which, for convenience, will be hereinafter designated by the expression "normal magnesium carbonate trihydrate" or by the corresponding formula, which is the more generally accepted designation of the substance. These crystals also set if subjected to elevated temperatures, above about 100° F., the rate of setting increasing as the temperature increases. Thorough agitation during carbonation, provided the temperature is kept low, favors the formation of the self-setting crystals or of the pentahydrate crystals which are also self-setting apparently by conversion during heating to the needle-like trihydrate crystals. These facts also account for the prior general use of slurries having great dilution, since ordinarily the bubbling of the carbon dioxide gas through the slurry was relied upon to effect agitation thereof. To effect proper agitation to insure the production of the self-setting crystals, it was necessary to use large amounts of carbon dioxide gas, and the use of such a large amount of gas, since the reaction is exothermic, produced an increased amount of heat, the necessity for the absorption and dissipation of which in turn led to the use of a large amount of water during the carbonation.

As stated previously, it is highly important

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that the temperature of the reaction be kept low and that adequate agitation be provided in the reaction medium. Electrolytic or colloidal substances, such as finely-divided particles of bentonite, may be added to act as nuclei for initiating the crystallization of the normal magnesium carbonate, but since such devices are not necessary for efficient crystallization, it is preferred not to employ them.

Figures 5 and 6 illustrate the effect of the carbon dioxide concentration in the carbonating gas. In Figure 5, the slurries employed contained 12.35 parts by weight of water to 1 part by weight of magnesium oxide, and the carbonating gas was introduced at such a rate that 7.5 cubic feet of carbon dioxide per hour per pound of magnesium oxide were passed through the slurries. The concentrations of carbon dioxide in the carbonating gas were for curve A, 50%; for curve B, 30%; and for curve C, 15%. In Figure 6, a gas composed of substantially 100% of carbon dioxide was introduced at the rate of 60 cubic feet of carbon dioxide per hour per pound of magnesium oxide into a slurry having a concentration of 12.35 parts by weight of water to 1 part by weight of magnesium oxide, and shows that introduction of a highly concentrated carbon dioxide at too rapid a rate causes the formation of the bicarbonate near the completion of the reaction. Figure 7 shows the effect of the rate of flow of the carbonating gas. In the slurries shown in Figure 7, a mixture of air and carbon dioxide gas in equal amounts by volume was passed through slurries having a concentration of 1 part by weight of magnesium oxide in 12.35 parts by weight of water. In curve A, the gas was introduced at 15 cubic feet per hour per pound of magnesium oxide in curve B, at a rate of 30 cubic feet per hour per pound of magnesium oxide, in curve C, at a rate of 45 cubic feet per hour per pound of magnesium oxide. It should be noted in connection with these curves that the reaction was completed in a shorter time with the formation of a considerably less amount of the bicarbonate in the early stages of the reaction when a higher rate of gas introduction was used.

While any dilute carbon dioxide may be employed in my process without danger of forming magnesium bicarbonate by excessive carbonation, it is preferred to use a gas which has a relatively low content of carbon dioxide, so that a great quantity of the gas may be passed through the slurry without generating an excessive amount of heat by virtue of reaction of carbon dioxide with magnesium oxide. By using such a dilute gas, thorough agitation of the reacting mass is effected, while, at the same time, the increased concentration of magnesium oxide is offset by the dilute concentration of the carbon dioxide, thereby effecting a proportionately greater amount of agitation for a given weight of carbon dioxide introduced into the reaction medium. Furthermore, the passage of the inert gases not taking part in the reaction through the reaction medium also assists in the dissipation, by convection and conduction, of the heat generated by the reaction. Any form of dilute carbon dioxide-containing gas is suitable, and as sources of such gases, there may be mentioned stack gases, the gases resulting from commercial alcohol processes, etc. The gas may be artificially produced. For example, carbon dioxide from a relatively concentrated source may be mixed with air or other available inert gas. This mixing may be effected just prior to introduction of the gas into the reaction medium by any suitable means, such as by means of an injector in which the passage of a stream of carbon dioxide flowing at high velocity is caused to entrain air just outside the reaction vessel. Similarly, a gas of relatively high concentration of carbon dioxide can be introduced into the reaction medium in close proximity to the point of introduction of inert gases, such as air, nitrogen, etc. While it is preferred to use a dilute carbon dioxide-containing gas, yet a relatively concentrated carbon dioxide-containing gas may be employed without excessive rise in temperature and without the formation of magnesium bicarbonate by excessive carbonation, provided it is introduced at a relatively slow rate. However, this involves a loss of time and, to obtain the best results, practically necessitates the employment of additional agitation, either by the introduction of an inert gas or by mechanical means. While a water jacket may be provided upon the apparatus for carbonating the slurry, it is preferred to avoid entirely any necessity to lower the reaction temperature by such means by properly controlling the conditions within the reaction system as aforesaid. The preferred embodiment of my invention, therefore, employs a dilute carbon dioxide-containing gas which functions not only by reacting with the magnesium oxide or magnesium hydroxide of the slurry to produce the desired self-setting crystals, but also by dissipating the heat and by agitating the reaction mass thereby eliminating the necessity of supplying the reaction vessels with water jackets and agitating means of a mechanical nature.

To facilitate the control of the carbonation conditions in concentrated slurries of magnesium oxide and of magnesium hydroxide in accordance with my invention, I have devised the apparatus illustrated in Figures 1 and 2. The reaction vessel comprises the casing 2, preferably of cylindrical shape, terminating at the bottom in the form of a truncated cone 3, having a slope inclined at such an angle that any crystalline material tending to settle out during the reaction will not stick to the bottom but will fall to the central portion of the reaction vessel. A suitable angle of inclination is one of 60° with the horizontal. A tube 4 is suspended within, and is preferably concentric with, the vessel so that its lower extremity forms with the conical wall 3 a narrow channel for the passage of the slurry therebetween. This tube is provided with upper and lower external spiders 5 and 6 respectively to maintain the tube properly centered and to act as a guide to assist the withdrawal of it from the vessel and it is provided with an internal spider 7 to maintain the pipe 8 in the center thereof. The length of the tube 4 is less than half that of the casing 2 so that the tube is well below the surface of the slurry and can be raised to a position within the casing entirely above the slurry therein. The cover 9 of the vessel is provided with a central opening through which the tube 8 extends down to the bottom of the reaction vessel. The cover also has an opening through which a chain 10 attached to the top of tube 4 can be pulled to a suitable hook 11, thus providing for adjustably positioning the tube 4 within the vessel. Instead of the hook 11, any suitable means for adjusting the position of tube 4 within the vessel may be provided, such as a winch with a ratchet arranged to prevent or to permit the centering of the tube 4 when the respective movements are desired. The opening in

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the cover 9 through which the chain 10 extends may also be provided with a sealing means, such as a tube of felt or sponge rubber to prevent passage of gas therethrough. The cover 9 is provided with an outlet pipe 12 (which may be connected to the gas inlet pipe of a second carbonator) to permit the outflow (and subsequent use) of any excess gases. The cover 9 is also provided with a manhole 13 to permit the introduction of reactants. Of course, all the openings in the vessel are preferably provided with suitable gaskets or packings to make the vessel gas-tight. If desired, the vessel may also be provided with a jacket 14. The bottom of the vessel is provided with a valve 15 opening into an outlet pipe 16 to permit the removal of the products of the reaction.

In operation of the carbonator, the carbon dioxide-containing gas is directed through the pipe 8, and it flows out through openings in the side or at the end thereof into the space generally surrounded by the tube 4. The flow of the gas upward within the tube 4 carries with it that portion of the slurry already within the tube and also sucks into the bottom of the tube the slurry immediately surrounding the tube at that point. As the slurry containing the gas flows upwardly through the tube 4 there is a circulation produced in the vessel in which the flow of slurry is continuously upwards within tube 4 and then downwards between the walls of tube 4 and the casing 2. The shape of the bottom 3 of the reaction vessel, together with the sweeping action of the current produced by the gas flow, prevents any deposition of sediment of magnesium oxide, magnesium hydroxide, or self-setting crystals thereon, and provided for effective and intimate mixing of the several components of the mixture. This prevention of settling out of solids is important in that such a settling involves a change of effective concentration of the magnesium oxide in the main body of the slurry tending to make it more dilute and thus increasing the risk of formation of the undesired magnesium bicarbonate toward the end of the reaction. The presence of the pipe 8 in the center of the reaction vessel extending above the tube 4 accentuates the particular circulating current by virtue of a certain tendency of the mixture of the gases and the liquid flowing upwardly to cling, possibly by virtue of surface tension, to the pipe 8, thereafter flowing outwardly and downwardly around the inside walls of the reaction vessel. The arrangement of tube 4 provides for adequate agitation even with relatively small amounts of gas, and the circulation prevents localized rise of temperature to an excessive degree.

A plurality of the carbonators may be operated at once by suitably connecting them by means of manifolds for supplying them with gas and also for permitting the efflux of the unused gas. Obviously the carbonators may be connected either in series or in parallel, but it is preferred that they be provided with suitable manifold and by-pass connections so that the gas flows in sequence through each carbonator from one to the next and so on, and so that the connections to any carbonator may be closed to permit the withdrawal of the reacted mass therefrom when the carbonation therein is complete without interrupting the introduction of the gas in sequence to the other vessels connected in series.

Carbonation of the mass under the conditions specified above is continued until substantially all of the magnesium compound content is converted to the self-setting crystals of either the tabular pentahydrate or the needle-like trihydrate crystals, and by opening the valve 15 the reacted slurry may be withdrawn into any suitable container or containers, or, if desired, directly into molds of the proper shape in which it may be allowed to set in accordance with the process hereinafter described.

While the product obtained from the setting of the self-setting crystals alone is suitable as a heat insulation medium, additional strength is obtained by incorporating therein from 10% to 15% of fibers, such as asbestos. Whereas the processes heretofore employed necessitated the addition of at least small amounts of alkaline materials, such as MgO, borax, caustic soda, or lime, to the slurry of self-setting crystals to make the slurry markedly alkaline and to absorb CO_2 given off from $Mg(HCO_3)_2$ in order to prevent the formation of fissures in the formed blocks, it has been found that blocks made in accordance with the process of the invention are substantially free of fissures and generally are somewhat harder and stronger, without the additional amounts of MgO or alkali, than those obtained when the alkaline materials are added. While not necessary, nevertheless, a certain amount of magnesium oxide or magnesium hydroxide may be added to the slurry of self-setting crystals prior to the setting thereof. This material may be added in any amounts from as low as 1% based on the weight of the trihydrate crystals up to as high as 30% or more in the manner and for the purposes suggested in United States Patent 2,209,754 and German Patent 528,134.

The fibers or the additional magnesium oxide or both may be added to the mixture in the carbonator just prior to the end of the time necessary to substantially completely convert the initial content of magnesium oxide to the self-setting crystals. For example, the addition may be made at any time after the conversion of at least about 95% of the magnesium oxide to the self-setting crystalline form has taken place. The mixture may thereupon be made intimate by the agitation involved in completing the carbonation of the initial magnesium oxide content of the slurry. Alternatively, the fibers with or without additional magnesium oxide or other alkali may be incorporated into the completely converted slurry of self-setting crystals in a separate agitator operated mechanically or by means of the bubbling of the gas therein.

The mixture so prepared, either in the carbonator or in a separate mixing vessel, may be molded immediately or, in a preferred mode of procedure, may be first preheated to a temperature not in excess of about 140° F. This preheating may occur in the carbonator in which case, the water jacket may be supplied with hot water or with steam, or the preheating may be applied simultaneously with the mixing of the fibers or the additional magnesium oxide or both into the self-setting crystal slurry, either in a carbonator or in a separate mixer.

The composition, whether preheated or not, is preferably molded by pouring it into the forms having the proper shape, which are then subjected to an elevated temperature of about 180° F. until the mass has taken a preliminary set. The products at this stage contain from 80% to 88% moisture. The surfaces of the slurry in the molds that are exposed may be subjected during the setting to a highly humid atmosphere, preferably to a saturated steam. This minimizes any

slight tendency for the composition to shrink by virtue of evaporation of water therefrom. The setting of the slurry of crystals is preferably allowed to take place while the mass in the molds is in a quiescent state and subjected only to the normal pressure of the atmosphere. If increased density in the product is desired, the composition may be allowed to set in the form of pressed cakes obtained after the composition has had any desired amount of water removed therefrom by a filter press or by any other means.

The self-sustaining blocks resulting from the preliminary set in the molds may be removed therefrom and subjected to the final drying, which may take place advantageously at temperatures within the range from about 200° F. to 400° F.

The following examples are illustrative of the invention:

Example 1

A slurry containing 53.6 pounds of magnesium oxide in 660 pounds of water was introduced into the carbonator and a gas containing air and 30% by volume of carbon dioxide was passed through the slurry for a period of two hours, the temperature during the carbonation attaining but not exceeding about 50° F. The slurry obtained comprised tabular crystals predominantly. The tube 4 was elevated to a position above the slurry and 18.8 pounds of asbestos fibers were added, carbonation being continued only sufficiently to obtain intimate mixing of the fibers into the slurry of crystals. The mixture was thereupon poured into molds, which were heated to 180° F. to preliminarily set the slurry in the forms, after which the set forms were removed and the product dried at 280° F. for a period of about 20 hours. The finished block had a density of 11.1 pounds per cubic foot and was firm, hard, and strong.

Example 2

A slurry of 53.6 pounds of magnesium oxide in 660 pounds of water was carbonated with a gas containing 25% carbon dioxide for a period of two hours. During the carbonation the temperature attained but did not exceed about 70° F. The crystals of the product were divided about evenly between the needle-like form and the tabular form. Carbonation was continued during the addition of about 5 pounds of magnesium oxide and 19 pounds of asbestos fibers until the additions were incorporated intimately therewith. The slurry of crystals was preheated to a temperature of about 140° F. and it was then poured into molds. The slurry cast in the molds was heated to about 180° F. until the several castings took a preliminary set, after which they were dried at 280° F.

Figure 3 illustrates one embodiment of the invention in general outline. In general, the procedure therein shown involves the making of a slurry of magnesium oxide in water, which is then carbonated at a temperature not over 100° F. Just prior to the completion of the carbonation of the initial magnesium oxide, additional magnesium oxide (if it is to be used) and the desired amount of fibers are added so that the product of the carbonation step is a mixture of normal magnesium carbonate trihydrate crystals with fibers with or without magnesium oxide. This slurry is preheated to 140° F. and then cast in forms where it is heated at 180° F. until set. The set forms are then dried at 200° F. to 400° F.

The products obtained have a glossy surface and are relatively hard, firm, and strong when considering their extremely light weight. The blocks or other bodies formed in accordance with the invention by quiescent setting without pressure have weights averaging from about 7 to 12 pounds per cubic foot. The products have a very low coefficient of heat conductivity, the structure of the blocks being highly cellular though the greater proportion of the cells are too small to be readily visible to the naked eye. All of the blocks are free of fissures, while those containing the additional magnesium oxide exhibit a surface which becomes less and less glossy, the higher the content of magnesium oxide in the block.

As stated previously, the wet self-setting crystals even in the cold are slowly converted to basic magnesium carbonate lacking the setting properties of the crystals. This partial conversion is followed by a disintegration of the particles upon agitation of the slurry containing the partially converted crystals. It is believed that this disintegration accounts for a corresponding weakening of the bond and an increase in the density in the final article made by prior processes, the latter defect being attributable to the filling of the voids between the crystals with the finely divided set particles torn off by the agitation of the crystals. My process, in which the steps of removing water and then reconstituting the crystals into a fresh quantity of water to form a slurry of uniform consistency are eliminated, reduces such disintegration to a minimum by reducing the amount of agitation and the time between the stages of complete formation of the self-setting crystals and the stage of quiescent setting in the molds. This fact, combined with the fact that the temperature during carbonation is maintained as low as possible by control of carbonation conditions, is thought to contribute fundamentally to the production of the stronger and lighter product which is remarkably free of friability and brittleness which characterized the products heretofore made by comparable processes.

While the invention has been disclosed in terms of specific examples employing certain materials in definitely stated proportions, the description is intended to be merely illustrative. Furthermore, it is not intended to limit this invention to any particular theories expressed. It is obvious that various modifications may be made without departing from the spirit of the invention and it is to be understood that the invention is limited only by the appended claims.

I claim:

1. In the method of making molded basic magnesium carbonate compositions, the steps of preparing a slurry of a magnesium compound selected from the group consisting of magnesium oxide and magnesium hydroxide, the initial concentration of the slurry being such that there are from approximately 9 to approximately 14 parts by weight of water for each part by weight of said magnesium compound based on its MgO content, introducing therein carbon dioxide gas while maintaining the said slurry at a temperature below 100° F. until substantially all of said magnesium compound is converted to self-setting hydrated crystals of normal magnesium carbonate, thereafter depositing said self-setting crystals, undiluted above approximately 14 parts of water for each part of said magnesium compound based on its MgO content, into a form, heating the slurry to effect setting of said self-setting crystals, and drying the set product.

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EXAMINEI

2. In the method of making molded basic magnesium carbonate compositions, the steps of preparing a slurry of finely divided magnesium oxide suspended in water in such a concentration that there are from 9 to 14 parts by weight of water for each part of magnesium oxide, introducing therein a gas containing not more than 50% by volume of carbon dioxide at a rate of flow at least as great as 7.5 cubic feet of carbon dioxide per hour per pound of magnesium oxide while removing exothermic heat and maintaining said slurry at a temperature below 100° F. until substantially all of said magnesium oxide is converted to self-setting hydrated crystals of normal magnesium carbonate, thereafter pouring said slurry of said self-setting crystals, undiluted above approximately 14 parts of water for each part of said magnesium compound based on its MgO content, into a form and causing the slurry to set, and removing the set product from the mold and heating to an elevated temperature to remove water and form such a molded basic magnesium carbonate composition.

3. In the method of making molded basic magnesium carbonate compositions, the steps of preparing a slurry of a magnesium compound selected from the group consisting of magnesium oxide and magnesium hydroxide in water, the initial concentration of the slurry being such that there are from approximately 9 to approximately 14 parts by weight of water for each part by weight of said magnesium compound based on its MgO content, introducing therein carbon dioxide gas while maintaining the said slurry at low temperatures below 100° F. until substantially all of said magnesium compound is converted to self-setting crystals generally represented as normal magnesium carbonate, thereafter forming said slurry of self-setting crystals in water so produced into the desired shape, and heating the slurry to cause it to set.

4. In the method of making molded basic magnesium carbonate compositions, the steps of preparing a slurry of a magnesium compound selected from the group consisting of magnesium oxide and magnesium hydroxide in an amount of water between approximately 9 and approximately 14 times the weight of the MgO content of said compound, introducing therein carbon dioxide gas and controlling the rate of introduction of carbon dioxide to keep said slurry at low temperatures below 100° F. until substantially all of said magnesium compound has been converted to self-setting crystals generally represented by the formula $MgCO_3nH_2O$ where n is selected from the group 3 and 5, thereafter pouring the slurry of self-setting crystals in water so produced into a form, heating the slurry to cause it to set, and drying the set product.

5. In the method of making molded basic magnesium carbonate compositions, the steps of preparing a slurry of a magnesium compound selected from the group consisting of magnesium oxide and magnesium hydroxide, the initial concentration of the slurry being such that there are from approximately 9 to approximately 14 parts by weight of water for each part by weight of said magnesium compound based on its MgO content, introducing therein a gas containing carbon dioxide in dilute concentration to maintain said slurry at low temperatures below 100° F. until substantially all of said magnesium compound is converted to self-setting crystals generally represented by the formula $MgCO_3.nH_2O$ where n is selected from the group 3 and 5, thereafter forming into the desired shape said self-setting crystals so produced, suspended in approximately 9 to approximately 14 parts by weight of water for each part by weight of said magnesium compound based on its MgO content, heating the slurry to cause it to rapidly set, and drying the set product.

6. In the method of making molded basic magnesium carbonate compositions, the steps of preparing a slurry of a magnesium compound selected from the group consisting of magnesium oxide and magnesium hydroxide in an amount of water between approximately 9 and approximately 14 times the weight of the MgO content of said compound, introducing therein carbon dioxide gas while maintaining said slurry at low temperatures below 100° F. until substantially all of said magnesium compound is converted to self-setting crystals generally represented by the formula $MgCO_3.3H_2O$, thereafter depositing said self-setting crystals in approximately the quantity of water in which said self-setting crystals were formed and undiluted above approximately 14 parts of water for each part of said magnesium compound based on its MgO content, into a form, heating the slurry to effect setting of said self-setting crystals, and drying the set product.

7. In the method of making molded basic magnesium carbonate compositions, the steps of preparing a slurry of a magnesium compound selected from the group consisting of magnesium oxide and magnesium hydroxide in an amount of water between approximately 9 and approximately 14 times the weight of the MgO content of said compound, introducing therein carbon dioxide gas while maintaining said slurry at low temperatures below 100° F. until at least approximately 95% of said magnesium compound is converted to self-setting crystals generally represented by the formula $MgCO_3.nH_2O$ where n is selected from the group 3 and 5, incorporating asbestos fibers into said slurry while continuing the introduction of a gas containing carbon dioxide to effect intimate mixing of said fibers into the slurry and to complete conversion of substantially all of said magnesium compound to the self-setting crystal form, thereafter pouring the slurry of self-setting crystals and asbestos fibers so produced into a form, heating the slurry to cause it to rapidly set, and drying the set product.

8. In the method of making molded basic magnesium carbonate compositions, the steps of preparing a slurry of a magnesium compound selected from the group consisting of magnesium oxide and magnesium hydroxide, the initial concentration of the slurry being such that there are from approximately 9 to approximately 14 parts by weight of water for each part by weight of said magnesium compound based on its MgO content, introducing therein carbon dioxide gas while maintaining said slurry at low temperatures below 100° F. until substantially all of said magnesium compound is converted to self-setting crystals generally represented by the formula $MgCO_3.nH_2O$ where n is selected from the group 3 and 5, heating the slurry of self-setting crystals to a temperature not in excess of 140° F., thereafter forming into the desired shape said slurry of self-setting crystals in water so produced, heating the formed slurry to effect rapid setting of said self-setting crystals, and drying the set product.

9. In the method of making molded basic magnesium carbonate compositions, the steps of preparing a slurry of a magnesium compound se-

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lected from the group consisting of magnesium oxide and magnesium hydroxide in an amount of water between approximately 9 and approximately 14 times the weight of the MgO content of said compound, introducing therein carbon dioxide gas while maintaining said slurry at low temperatures below 100° F. until at least 95% of said magnesium compound is converted to self-setting crystals generally represented by the formula $MgCO_3.3H_2O$ incorporating additional magnesium oxide and asbestos fibers while continuing the introduction of said gas to effect intimate mixing of said oxide and fibers into the slurry and to complete the conversion of substantially all of the initial magnesium compound to the self-setting crystal form, heating the slurry of self-setting crystals to a temperature not in excess of 140° F., thereafter pouring the slurry of self-setting crystals in water so produced into a form, heating the slurry in the form to cause it to rapidly set, removing the set product from the mold, and drying the set product at an elevated temperature.

10. In the method of making molded basic magnesium carbonate compositions, the steps of preparing a slurry of a magnesium compound selected from the group consisting of magnesium oxide and magnesium hydroxide in an amount of water between approximately 9 and approximately 14 times the weight of the MgO content of said compound, introducing into said slurry carbon dioxide gas while maintaining the slurry at low temperatures not in excess of approximately 50° F. until substantially all of said magnesium compound is converted to self-setting crystals generally represented by the formula $MgCO_3.5H_2O$, heating the slurry of self-setting crystals to a temperature not in excess of 140° F., thereafter depositing said self-setting crystals so formed suspended in approximately 9 to approximately 14 times their weight in water into forms, heating the slurry to cause it to rapidly set, and drying the set product.

11. In the method of making molded basic magnesium carbonate compositions, the steps of preparing a slurry of a magnesium compound selected from the group consisting of magnesium oxide and magnesium hydroxide in an amount of water between approximately 9 and approximately 14 times the weight of the MgO content of said compound, introducing therein carbon dioxide gas while maintaining said slurry at low temperatures below 100° F. until substantially all of said magnesium compound is converted to self-setting crystals generally represented by the formula $MgCO_3.3H_2O$, heating the slurry of self-setting crystals at a temperature not in excess of 140° F., pouring the slurry of self-setting crystals in water so produced into a form, heating the slurry in the form to cause it to rapidly set, removing the product from the form, and drying the set product.

12. In the method of making molded basic magnesium carbonate compositions, the steps comprising preparing a slurry of magnesium oxide containing approximately 9 to approximately 14 parts by weight of water for each part by weight of magnesium oxide, introducing therein a gas containing not more than 50% by volume of carbon dioxide at a rate of flow at least as great as 7.5 cubic feet of carbon dioxide per hour per pound of said magnesium oxide while maintaining the said slurry at a temperature below 100° F. and continuing the introduction of said gas until substantially all of said magnesium oxide is converted to self-setting hydrated crystals of normal magnesium carbonate, whereby the slurry as so formed may be deposited into a mold without filtration or resuspension, set therein, and subsequently dried.

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