Patented Sept. 27, 1938

2,131,374

UNITED STATES PATENT OFFICE

2,131,374

DOLOMITIC MAGNESIUM CARBONATE COMPOSITION AND METHOD OF PREPARATION

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No Drawing. Application August 17, 1936, Serial No. 96,474

11 Claims. (Cl. 25—156)

The invention relates to magnesium carbonate compositions of the type suitable for insulating purposes, and more particularly to an improved composition of this character made from dolomitic material as the source of raw material, in which the compounds of calcium derived from the dolomitic material are not removed or separated for the purpose of providing a final product of the requisite degree of lightness, strength and insulating properties, but remain in the final product, and also to an improved process for producing such composition whereby the composition has the property of self or hydraulically setting without shrinkage. This application is a continuation in part of the co-pending application Serial No. 717,077, filed March 23, 1934.

Magnesium carbonate compositions are used in sound and heat insulating and similar products, and although they can be made directly from magnesite or other sources consisting essentially of magnesium compounds, the source of raw material, in this country at least, is primarily true dolomite or similar dolomitic material such as dolomitic limestones, containing both magnesium and calcium compounds, primarily in the form of carbonates. This is so because the supply of dolomitic material in this country is much greater than that of material composed primarily of magnesium compounds; the latter material being commercially available only on the west coast of the United States in the States of California and Washington. Practically 85% of the magnesium carbonate compositions manufactured in this country are made from dolomitic material as the source.

For use in insulating products, magnesium carbonate compositions must meet certain commercial specifications as to weight, strength and insulating properties, the latter, of course, being partially a function of the weight because the more dense the product the less porous it will be. In order to satisfy such specifications, other commercial processes require that the calcium compounds be eliminated in the preparation of the final magnesium carbonate composition when dolomitic material is the source of raw material. Such elimination step obviously involves considerable expense, and as a result increases the cost of manufacture of the product from dolomitic material as the source.

In the preparation of the magnesium carbonate composition by other processes, it is the general practice to gas an aqueous suspension of calcined dolomitic material with carbon dioxide-containing gas to precipitate calcium carbonate which remains insoluble. Magnesium carbonate also precipitates out, but the gassing is continued to such an extent as to convert the magnesium compounds to form magnesium bicarbonate which is water soluble, to thus enable the insoluble calcium carbonate to be separated from the magnesium bicarbonate solution by filtration or other suitable way. Subsequently, a precipitate of basic magnesium carbonate is obtained by heating the solution of the magnesium bicarbonate.

In such other methods, it is necessary in order to form the resultant magnesium carbonate in blocks or slabs of the desired shape and size, to mold the product in suitable forms under relatively high mechanical pressure because the magnesium carbonate lacks self-setting properties i. e., it cannot undergo a hydraulic set. This molding equipment is expensive to maintain and operate as well as to construct. Furthermore, because of the pressure applied during the molding, the product is compacted and consequently made more dense than would occur in a corresponding product having self-setting properties. This is another reason, why, in addition to the greater weight of the calcium carbonate compared to that of magnesium, the calcium compounds have to be removed in other present commercial processes.

The invention is designed to overcome the above described problems heretofore encountered in the manufacture of magnesium carbonate compositions from dolomitic material as the source, and has as objects among others, the provision of an improved:

(1) Light weight, yet strong magnesium carbonate composition from dolomitic material as the source, in which substantially all of the calcium occurring in such source in the form of a compound, remains in the final composition or product in the form of a calcium compound;

(2) Composition, of the character related, having self or hydraulic setting properties;

(3) Composition, of the character related, having improved insulating properties, and which can be economically produced; and

(4) Process for obtaining such composition from dolomitic material.

Other objects of the invention will become apparent from a perusal of the following description thereof.

In general, it has been found that during gassing of an aqueous suspension of calcined dolomitic material, with carbon dioxide-containing gas, calcium carbonate is first formed as a preci-

pitate, and then upon continued gassing, a precipitate of comparatively thin, needle-like crystals of a carbonate of magnesium is formed. If a slurry containing the precipitated calcium carbonate and the thin, needle-like carbonate of magnesium crystals is cast or poured into a form or mold, the composition will set in a quiescent state without application of mechanical pressure thereto, to provide the strong, and light weight self-setting product of the invention. The setting in the mold is enhanced by application of heat.

In other words, it has been found that when the described aqueous suspension of calcined dolomitic material is gassed with carbon dioxide-containing gas to the point where, in addition to the insoluble calcium carbonate precipitate, there is formed a carbonate of magnesium in the form of comparatively thin, needle-like crystals, especially crystals resulting from the reaction of the carbonate radical with the magnesium ion in an aqueous vehicle, the resulting composition has self or hydraulic setting properties rendering it unnecessary to mold the composition under pressure to form slabs or blocks. Thus, compacting of the material does not obtain, which, in other methods, increases the density of the final product, thereby necessitating the removal of the calcium compounds in order to provide a product of the requisite strength, lightness and insulating qualities.

Although the dolomitic magnesium carbonate composition of the invention has the property of self-setting in a quiescent state without application of pressure thereto, and this is the manner employed by this invention for producing the product, it will also set if pressure is applied as in other methods and still produce a stronger product than could be obtained by such other methods. Inasmuch as pressure molding is necessary to produce a satisfactory product by other methods and because pressure may be applied to the composition of the invention but is not necessary, the expression "independent of pressure" is employed hereinafter to describe that the composition of the invention has self-setting properties not conditioned on pressure.

The self-setting principle is imparted to the composition by the particular nature of the carbonate of magnesium crystals formed during the gassing with the carbon dioxide-containing gas; one of the important factors being to avoid as much as possible transformation of the water insoluble carbonate of magnesium to the water soluble magnesium bicarbonate by the addition of excess carbon dioxide. If this were done to a material extent, magnesium carbonate could only be obtained again by heating which destroys the self-setting properties. The Canadian Patent No. 328,196, granted December 6, 1932, discloses the method of obtaining a self-setting carbonate of magnesium where a straight magnesium compound, such as magnesite, is the source of raw material.

It is desirable, during the gassing of the aqueous suspension of the magnesium and the calcium hydroxides which are formed by reaction between the water and the calcined dolomitic material which, because of the calcining, consists essentially of calcium and magnesium oxides, and especially during formation of the needle-like crystals of the carbonate of magnesium after the calcium carbonate is precipitated, that the reaction be carried on under vigorous or excessive agitation, either mechanical or that obtained by the gassing with the carbon dioxide-containing gas or both. Such agitation is preferable to obtain complete reaction between the magnesium and carbonate ions, and to form as small and as thin crystals of the carbonate of magnesium as can be practically obtained because the smaller and thinner the crystals, the stronger the final product. Agitation enhances the formation of the desired type of crystals. It is believed that with small thin crystals there is a greater interlacing thereof to provide a firmer bonding of the calcium carbonate by the carbonate of magnesium upon setting of the composition.

Also for best results, the reaction should be so controlled, in addition to the agitation, as to convert substantially all of the magnesium compounds present in the reacting medium, to the described crystalline carbonate of magnesium, to thereby obtain a maximum yield of the comparatively thin, needle-like carbonate of magnesium crystals from the magnesium source. This is so because the presence of other magnesium salts admixed with the crystalline carbonate of magnesium impairs the self-setting properties of the composition and the strength of the final product, while the presence of magnesium bicarbonate solution retards setting and impairs strength.

Another important factor in obtaining the proper type of comparatively thin, needle-like carbonate of magnesium crystals having self-setting properties, is temperature control prior to the setting of the composition in molds. At too high a temperature prior to molding, the crystals are altered or transformed from crystals of comparatively thin, needle-like character to comparatively fat crystals which do not possess satisfactory self-setting properties. Therefore, during formation of the carbonate of magnesium crystals by the carbon dioxide-containing gas, the temperature should be controlled to avoid this transformation.

Subsequent to the precipitation of the water insoluble calcium carbonate which remains practically insoluble irrespective of how long the gassing is continued, and after formation of the self-setting carbonate of magnesium needle-like crystals in the aqueous vehicle, excess water is removed by decantation or any other suitable method; and the remaining aqueous slurry, containing calcium carbonate admixed with the carbonate of magnesium crystals, is ready for setting. After such slurry is prepared, and during the period prior to the step of setting the slurry, agitation should be avoided as much as possible because such agitation will increase the density of the final product and lessen the bonding power of the carbonate of magnesium crystals during setting thereof. In the setting operation, the described slurry is cast or poured directly into molds, which are preferably unperforated; and the molds are merely heated for a length of time and at a temperature sufficient to set the slurry or sludge to a firm cake. Agitation of the composition in the molds, is avoided because such agitation will impair the setting property of the carbonate of magnesium crystals. Hence, the setting in the molds is accomplished with the composition in a quiescent state.

The composition does not shrink upon setting and no pressure need be applied to the composition. Consequently, the density of the final product is governed by the quantity of water left in the slurry which is poured into the molds. During the setting, it is believed that carbon dioxide

gas is evolved; and microscopic observation shows that the carbonate of magnesium crystals which were originally all comparatively thin or fine, needle-like crystals, now consist essentially of a mixture of two crystal forms. Some of the needle-like crystals remain, but a new, very small crystal appears. Such new crystal tends to cluster into grapelike groups, or to adhere to the surface of the needle-like crystals. This probably accounts for the great strength of the final product, which breaks with a clean or concholdal fracture in contradistinction to the product produced by other processes, which mushes upon being broken, thus indicating that the product of the invention is bonded by virtue of interlacing of the crystals. Because of the evolution of the carbon dioxide and the formation of the new crystals, it is believed that a reaction probably occurs in which some of the carbonate of magnesium is converted to magnesium oxide or magnesium hydroxide, thus forming a light type of magnesium carbonate which serves as the bonding medium for the calcium carbonate in the admixture.

No pressure is required to compact or mold the composition, as the composition sets in a quiescent state, but, as previously explained, pressure molding may be employed and still produce a superior or a special dense product for certain uses. However, such pressure molding is preferably omitted inasmuch as it would increase the density of the final product which, as previously explained, is heavier, than would otherwise be the case, by the presence of the calcium carbonate. The temperature applied to the molds during the setting should not be too high nor applied too rapidly, because, although the product will set, the evolution of gas would be so fast as to leave the final product full of gas holes. Neither should the temperature be too low, because then the setting would, generally speaking, be too slow. A suitable temperature range is substantially from 60° C. to 90° C. At this temperature range, the setting to a hard cake will usually occur in from one to three hours; the time varying of course with the temperature actually applied, and also with the character of the composition resulting from the particular dolomitic material employed. Preferably, the heating of the composition in the molds to facilitate the setting, is obtained by placing the molds in a chamber containing steam at the proper temperature.

The composition sets normally without shrinkage, which is important, because if material shrinkage were to occur, then of course its final shape could not be fixed by the mold and wasteful trimming would have to be employed to produce the desired shaped block or slab. Also, by not shrinking, the density of the composition is not increased during the setting thereof. This is important for controlling the final weight of the product, as determined by the original amount of water which is left in the slurry. Under some circumstances, slight shrinkage of the composition might occur, but not as much as the shrinkage which occurs in other commercial processes wherein mechanical pressure molding of the composition is absolutely necessary to produce a satisfactory product; it of course being understood that in the other commercial processes, where dolomitic material is used as the source of raw material, the calcium compounds are removed, as the molded product consists essentially of magnesium carbonate instead of the admixture of calcium carbonate with the carbonate of magnesium which the method allows.

After having set in the molds, the blocks or slabs which are formed are self-supporting before they are dried. Blocks or slabs formed in other commercial processes where pressure molding is employed and which consist essentially of magnesium carbonate without calcium carbonate, are not self-supporting, and consequently, have to be supported in frames during drying thereof. The method of the invention, therefore, eliminates the necessity of having to provide such frames to support the molded products. Upon removal of the slabs or blocks from the molds, they are next dried in the usual manner heretofore employed for drying the mechanically molded product, except that no frames are needed.

Such drying is accomplished usually in conventional drying ovens, at a temperature ranging from 70° C. to 200° C., to remove all uncombined or free moisture not existing as water of crystallization. Depending on the temperature, it will take from 24 to 72 hours for the drying. The drying, if desired, may be accomplished under atmospheric conditions, but oven drying is preferred because it is faster. Should the material tend to stick in the molds upon removal therefrom, the molds may be first greased with any suitable substance such as petroleum grease.

Even though there is no shrinkage of the material in the molds, it may be desirable to mill or trim the surfaces of the dry product so as to provide an attractive product not marred with surface imperfections. Not over 10% of the product need be removed by such milling, whereas with products produced by other methods wherein molding under pressure is required, the amount of product removed by milling runs from 30% to 40%. The milled off material is not entirely waste material because it may be used for making magnesia insulating cement. However, it has less value as a cement and therefore results in an economic loss. Hence, because of the lesser amount of material which need be trimmed from the block or slab of the invention, a further economy is effected. Because of the setting of the product of the invention in a quiescent state with substantially no shrinkage, the molds may be made of special shapes so as to form correspondingly shaped articles such as insulating fittings.

Although the product or composition of the invention contains calcium carbonate, in which all of the calcium originating from the source of dolomitic material exists, it is still light enough to permit incorporation therewith of the usual foreign materials employed in magnesium carbonate insulating products. For example, asbestos fiber, usually employed for reinforcing purposes, may be incorporated in the slurry containing the calcium carbonate precipitate and the carbonate of magnesium crystals. Also, diatomaceous earth may be incorporated in the slurry for the purposes of enabling the product to withstand higher temperatures.

Standard commercial preparations of magnesium carbonate insulating blocks produced by other methods contain about 85% by weight of magnesium carbonate as a bonding agent and about 15% by weight of asbestos fiber to reinforce the product. Under present standards, such blocks weigh from 16 to 18 lbs. per cubic foot; the specific gravity, therefore, ranges from about 0.256 to 0.288. The product of the invention containing the same percentage of asbestos fiber, and in which calcium carbonate is not

eliminated, or in other words, contains all of the calcium occurring in the source of dolomitic material, as a carbonate, can be made to weigh about 12 to 16 lbs. per cubic foot; the specific gravity, hence, ranging from about 0.192 to 0.256. In addition to lightness, the dolomitic product of the invention possesses greater strength and has higher insulating efficiency than the product produced by other commercial methods even though, in such other methods, the calcium compounds are eliminated from the source of dolomitic material. For example, a block of the invention weighing about 14 lbs. per cubic foot is stronger than a 16 lb. per cubic foot block produced by other commercial methods involving mechanical pressure and from which calcium carbonate is eliminated. Yet such block of the invention will have about a 25% greater insulating efficiency.

By virtue of the extremely light weight of the composition, it is highly porous, i. e., cellular in structure, which is one of the factors contributing toward its heat insulating efficiency. Furthermore, although the composition is shaped, it is not stony or rock like in appearance as are artificial stones or natural rocks such as the original dolomitic material from which it is essentially derived, but is chalk-like in character. In other words, compared to an artificial stone or natural rock, it is relatively crushable, and the material may be readily rubbed off from the surface thereof.

If, in other commercial processes employing dolomitic material as the source of raw material, the calcium compounds were not removed, then the final product would weigh too much to meet commercial specifications because of the material shrinkage which occurs during the molding, and the mechanical pressure necessary to effect molding, which mechanical pressure compacts the product. Also, such product would be very fragile; and because of increased density imparted by the calcium carbonate, would have unsatisfactory insulating efficiency.

From the preceding description, it is seen that one of the important features of the method resides in the formation, in the aqueous suspension of the calcined dolomitic material, of the carbonate of magnesium crystals having the self-setting properties, which, because of such self-setting properties, allow the calcium carbonate derived from the dolomitic material to remain in the final product without impairing its efficiency compared to products compacted by pressure molding and in which calcium carbonate is eliminated by necessity. The preferred process for obtaining such crystals will now be described.

Dolomite, which contains magnesium carbonate and calcium carbonate in the ratio of about 40 to 60, respectively, or any other dolomitic limestone, is first calcined in the usual manner to prepare oxides of these metals. As a result of the calcining, carbon dioxide gas is evolved, which may be subsequently used in the process during the gassing operation. However, if the plant does not have calcining facilities but purchases the calcined dolomitic material, stack gas or any other suitable carbon dioxide-containing gas may be employed during the gassing for carbonating purposes.

A comparatively dilute aqueous suspension of magnesium and calcium hydroxides is then prepared by slaking and mixing the calcined dolomitic material with water, preferably in the proportions of about 20 parts of water by weight to 1 part of the calcined dolomitic material by weight, although the proportions may vary widely from about 10 to 40 parts of water by weight to 1 part of the dolomitic material by weight. Too little water impedes the reaction of the magnesium compounds in the vehicle, with the carbon dioxide-containing gas, while too much water may be impractical as it involves the problem of subsequent separation of the water from the slurry containing the calcium carbonate and the carbonate of magnesium crystals. Also, upon introduction of the carbon dioxide-containing gas into the suspension, an exothermic carbonation reaction occurs; and for reasons subsequently related, it is desirable to prevent too high a reaction temperature. Therefore, the quantity of water should be sufficient to absorb as much of the heat of the gassing reaction as is practically possible. At the same time, it may be preferable to employ an outside cooling medium to prevent too high a heat of reaction. The preferred proportions of water are those which permit the optimum rate of reaction without undue creation of heat, and still provide a minimum quantity which is to be subsequently removed. Of course, the proportions may vary in accordance with the carbon dioxide concentration in the gas as well as the character of the dolomitic material.

Carbon dioxide-containing gas is next introduced into the aqueous suspension of the magnesium and calcium hydroxides, preferably into an open tank or vessel which contains the suspension. The calcium hydroxide has a greater affinity for the carbon dioxide than the magnesium hydroxide. As a result, the first reaction which occurs is the precipitation of water insoluble calcium carbonate which after once precipitated is not redissolved upon continued gassing.

After precipitation of the calcium carbonate, two major reactions occur, namely, the formation of water soluble magnesium bicarbonate and the formation of an insoluble carbonate of magnesium. These reactions are controlled more or less by temperature conditions, and the length of time of gassing. If the temperature is too low, the formation of the bicarbonate is favored. If the temperature is too high, the rate of reaction is too slow for commercial practicability.

As it is desired to produce the comparatively fine or thin, needle-like carbonate of magnesium crystals having the self-setting properties, the temperature for the precipitation of the carbonate of magnesium crystals should be maintained above the point below which the formation of magnesium bicarbonate is favored, because the presence of too great a quantity of the bicarbonate in the final gassed composition retards the setting properties of the carbonate of magnesium crystals. A suitable temperature range is between about 20° C. and 40° C., preferably at about 30° C. Since the reaction involved is exothermic, some cooling will probably be necessary to maintain this temperature range, depending upon the rate of reaction and the amount of water. In order to enhance the reaction and produce small size carbonate of magnesium crystals for the reasons previously explained, vigorous agitation is preferable. Mechanical agitation may be employed. However, it is preferred to effect the agitation through the introduction of the carbon dioxide containing gas with or without additional agitation.

The presence of magnesium in form other than the crystal form impairs the setting properties

of the composition. Therefore, a maximum yield of the carbonate of magnesium crystals should be obtained, after the calcium carbonate has been precipitated. To insure this maximum yield or complete carbonation of substantially all the magnesium in the form of the insoluble crystalline carbonate precipitate, over-gassing which results in the formation of the water soluble bicarbonate is avoided as much as possible; and the gassing is continued until the resulting precipitate of the carbonate of magnesium crystals starts to go into solution as magnesium bicarbonate, or, in other words, to a point not substantially beyond incipient solution of the carbonate of magnesium crystals.

At this end point, substantially all of the magnesium will be precipitated in the crystalline form, but upon continued or over-gassing a major reaction then occurs between the carbonate of magnesium and carbonic acid to form the undesirable water soluble magnesium bicarbonate. This end point can be determined by observation of the operator, and by chemical titration of selected samples because as the amount of bicarbonate increases beyond the end point, the amount of acid required to neutralize filtered samples from the batch increases. By slight over-gassing or carbonating slightly beyond the end point or, in other words, until the resulting carbonate of magnesium crystalline precipitate starts to go into solution, substantially complete carbonation is insured. If the gassing has been carried out too far beyond the desired end point, and if the composition has not been excessively over-gassed, the relatively small amount of the water soluble magnesium bicarbonate can be neutralized by the addition of magnesium oxide, to reprecipitate the desired carbonate of magnesium crystals from the magnesium bicarbonate in solution.

It is to be noted that in other commercial processes, the aqueous suspension of the calcined dolomitic material is completely overgassed. In other words, the gassing is carried on to convert all of the magnesium carbonate to the water soluble magnesium bicarbonate to permit separation of the calcium carbonate. Magnesium carbonate is subsequently precipitated from the bicarbonate solution by application of heat which in the process is avoided, as it destroys or impairs the self-setting properties of the carbonate of magnesium crystals. To facilitate this over-gassing in the other processes, gases containing relatively high percentages of carbon dioxide are employed to enhance the formation of the bicarbonate. Also, to enhance formation of the bicarbonate, the gas in such other processes is introduced into a closed vessel or tank which is consequently under pressure. It is known that the bicarbonate solution formation is favored by pressure. Since over-gassing is to be avoided in the process, gases containing much lower percentages of carbon dioxide and even stack gases which contain a low carbon dioxide content, may be employed in the process. Low carbon dioxide content gases cannot be employed in the other processes with practicability. Also, since over-gassing is avoided in the process, there is no necessity of gassing in a closed vessel under pressure and, as previously related, there is employed an open vessel during the gassing or carbonation. These facts result in further economy. Since the process permits the use of low content carbon dioxide-containing gas, in percentages as low as 6% by weight, this enhances the desired excess agitation to produce the desired type of carbonate of magnesium crystals, because a greater volume of gas has to be introduced to complete the reaction, compared to the volume which would be required when employing a concentrated gas which in other processes has run as high as 100% carbon dioxide.

After the introduction of carbon dioxide has been stopped at the desired point, the aqueous mixture containing the precipitated calcium carbonate and the carbonate of magnesium crystals, is allowed to stand, in a relatively quiescent state, for about an hour or two without application of heat which, as previously related, affects the setting properties of the carbonate of magnesium crystals if applied prior to the setting. During this period, the precipitate settles as a slurry or sludge, and a water layer forms at the top. Such layer of water starts to collect substantially immediately after the gassing is completed. The small quantity of magnesium bicarbonate in solution formed by the slight over-gassing, is converted to the carbonate of magnesium crystals by its own decomposition and by reaction with any existing small quantity of minute particles of magnesium hydroxide which might not have reacted during the gassing.

The resulting mass will be substantially neutral, and the precipitate will consist essentially of calcium carbonate intermixed with needle-like crystals of a carbonate of magnesium which produces the set. After standing for the desired time to allow settling of the slurry or sludge, excess water which collects above the slurry or sludge may be drained, or removed in any other suitable manner, such as by filtration; the amount of water in the slurry, as controlled by the quantity of excess water removed, determining the density of the final product inasmuch as the composition does not shrink on setting. The slurry at this point is ready for use in the preparation of the final product, such as heat insulating material, without further treatment except that occurring during the setting thereof. In this connection, the setting is carried out in the manner previously related, care being taken to avoid application of heat prior to the setting.

Analysis under the microscope reveals that the thin or fine needle-like carbonate of magnesium crystals which provide the self-setting composition of the invention, will vary in size from 20 to 50 microns in length and from 2 to 5 microns in thickness. In other processes, involving carbonation of magnesium compounds, crystals are formed but because of lack of vigorous or excessive agitation, they are much larger in size. However, such crystals are altered or transformed prior to molding, by subsequent steps of the processes, such as by application of heat prior to molding. In the method of the invention, the product or composition containing calcium carbonate intermixed with the thin, needle-like crystals of a carbonate of magnesium, is cast or poured directly into open molds or forms, to set, in a quiescent state, in the manner previously explained.

The aqueous slurry prepared as above described and containing substantially all the magnesium as a carbonate in the form of described crystals, and also the calcium carbonate, may be cast or poured into the molds as such, but in view of the light weight, strength, insulating properties, and setting properties of the final product, other materials desirable for incorporation in the manufacture of insulating materials, may be intermixed with the slurry. Preferably, if this is done,

such other materials are introduced into the slurry prior to the removal of excess water for adjusting or controlling the water content. In some cases, it might be desirable to even add water to such slurry where the other material absorbs in itself a lot of water. Usually, foreign materials, such as asbestos or diatomaceous earth, which will not detract materially from the heat insulating properties of the final product, are incorporated in the slurry. Upon setting, the carbonate of magnesium serves as the bonding agent for the foreign material incorporated therewith, as well as for the calcium carbonate. The slurry to which any of the above types of foreign materials may have been added and after the water content is adjusted or controlled, is poured into molds and allowed to set in a quiescent state in the manner already explained.

After setting and drying, the resulting product, although containing a very high proportion of calcium carbonate, is found to have, as was previously related, a higher mechanical strength and a lighter weight than the materials previously made from magnesium carbonate alone. This is so, even though all the calcium occurring as a calcium compound in the original source of dolomitic material, remains in the final product as calcium carbonate. Although the described process is preferred, it may be varied, as will be apparent to those skilled in the art from the teachings of the invention, in accordance with the character of raw material employed, the concentration of gas, the amount of water in the aqueous suspension, etc. It is only important that all of the magnesium compounds in the aqueous slurry be converted to the fine, needle-like carbonate of magnesium crystals, which it has been found will set hydraulically to bond the calcium carbonate and thereby provide the improved product of the invention, and that these crystals be not subsequently destroyed during further steps of the process; the factors pointed out above facilitating obtaining the desired type of crystals.

What is claimed is—

1. A composition derived essentially from dolomitic material and having self-setting properties comprising a slurry in which the major portion of the solid materials are calcium and magnesium compounds, the calcium compound in such slurry being calcium carbonate, and substantially all of the magnesium in such slurry being in the form of a crystalline carbonate of magnesium having self-setting properties.

2. The step in the method of producing from dolomitic material a composition having self-setting properties which comprises carbonating a suspension containing calcined dolomitic material to convert substantially all of the magnesium containing substance in such suspension to a carbonate of magnesium in crystalline form possessing self-setting properties.

3. The method of producing from dolomitic material a composition having self-setting properties which comprises carbonating an aqueous vehicle containing calcined dolomitic material to form water insoluble calcium carbonate and to convert substantially all of the magnesium containing substance in such vehicle to a water insoluble carbonate of magnesium in crystalline form, terminating the carbonation when substantially all the magnesium containing substance has been thus converted; and enhancing the setting by applying heat to a slurry containing said calcium carbonate and said crystalline carbonate of magnesium.

4. The method of producing from dolomitic material a composition having self-setting properties which comprises carbonating under agitation an aqueous vehicle containing calcined dolomitic material to convert substantially all of the magnesium containing substance in such vehicle to a carbonate of magnesium in crystalline form possessing self-setting properties, providing a desired density slurry of calcium carbonate derived essentially from said dolomitic material and said carbonate of magnesium by adjusting the water content of such slurry, casting said slurry into a form, and heating the slurry in the form to enhance setting of the composition.

5. The step in the method of producing a composition derived essentially from dolomitic material and set independent of application of pressure thereto which comprises heating a formed slurry containing calcium carbonate and a carbonate of magnesium in crystalline form having self-setting properties.

6. The method of producing a set composition from dolomitic material which comprises treating with carbon dioxide-containing gas an aqueous vehicle containing the calcined dolomitic material to precipitate calcium carbonate, controlling the conditions of treatment to convert substantially all of the magnesium containing substance in said vehicle to a self-setting carbonate in crystalline form, and heating in a quiescent state a slurry containing both said calcium carbonate and said crystalline carbonate of magnesium until it sets to a firm cake.

7. The method of preparing insulating material from dolomitic material as the source which comprises gassing an aqueous suspension of the calcined dolomitic material with carbon dioxide-containing gas to precipitate first calcium carbonate, continuing the gassing to precipitate next a carbonate of magnesium, controlling conditions of temperature to avoid formation of magnesium bicarbonate, stopping the gassing substantially at the time when incipient solution of said carbonate of magnesium to the bicarbonate occurs to obtain substantially a maximum yield of said carbonate of magnesium precipitate in the form of needle-like crystals having self-setting properties, removing excess water, casting the resulting slurry of the calcium carbonate and the carbonate of magnesium into a mold, applying heat to such slurry in the mold while in a quiescent state to effect setting of the slurry to a firm cake independent of application of pressure thereto, and subsequently drying said set cake.

8. The method of preparing a set composition from dolomitic material as the source which comprises carbonating a relatively dilute aqueous suspension of the calcined dolomitic material to precipitate calcium carbonate, continuing the carbonation to precipitate a carbonate of magnesium, maintaining the temperature of reaction above the temperature below which the formation of magnesium bicarbonate is favored and below the temperature above which the reaction proceeds too slowly, terminating the carbonation substantially at the time when incipient solution of said carbonate of magnesium to the bicarbonate occurs to obtain substantially a maximum yield of said carbonate of magnesium precipitate in the form of relatively thin needle-like crystals having self-setting properties, removing excess water to provide a slurry of the desired density, prior to any application of heat to such slurry casting it into a mold without removing the calcium carbonate therefrom, ap-

plying heat to such slurry in the mold while in a quiescent state and without application of pressure thereto to effect setting of the slurry to a firm cake, and subsequently drying the cake.

9. The method of producing from dolomitic material a composition having self-setting properties which comprises carbonating an aqueous suspension containing calcined dolomitic material to form calcium carbonate and to convert substantially all of the magnesium substance in such suspension to a carbonate of magnesium in crystalline form possessing self-setting properties, incorporating in said carbonated suspension foreign material of the class consisting of asbestos and diatomaceous earth to impart desired properties to the final product, providing a desired density slurry by adjusting the water content, and setting such slurry to a firm cake by applying heat thereto.

10. A light weight cellular chalk-like composition capable of use as a heat insulating material containing modified dolomitic material in which substantially all of the calcium in the original dolomitic material is present as calcium carbonate and which is bonded by a magnesium compound derived from needle-like crystals of a carbonate of magnesium having self setting properties, said magnesium bonding compound containing magnesium derived from said original dolomitic material.

11. A light weight cellular chalk-like composition set substantially without shrinkage independent of application of pressure and capable of use as a heat insulating material, containing fiber to reenforce the composition, and modified dolomitic material in which substantially all of the calcium in the original dolomitic material is present as calcium carbonate and which is bonded by a magnesium compound derived from needle-like crystals of a carbonate of magnesium having self-setting properties, said magnesium bonding compound containing magnesium derived from said original dolomitic material.

DOROTHY H. GRUNWALD,
Administratrix with the Will Annexed of the Estate of Bertrand B. Grunwald, Deceased.

Patented July 30, 1940 2,209,752

UNITED STATES PATENT OFFICE

2,209,752

MAGNESIUM CARBONATE COMPOSITION AND PROCESS FOR THE PREPARATION THEREOF

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No Drawing. Application June 9, 1938, Serial No. 212,696

2 Claims. (Cl. 23—67)

Our invention relates to magnesium carbonate compositions, and more particularly to an improved magnesium carbonate composition which has the property of self or hydraulically setting substantially without shrinkage, and also to an improved process for producing such self-setting composition.

Magnesium carbonates are used in sound and heat insulating and similar materials, and have generally comprised either the heavy basic carbonate or the light basic carbonate, or modifications of these materials. These basic carbonates have been prepared by various methods. One form of commercial process for manufacturing such basic carbonates, where dolomitic material is the source of raw material and it is desired to eliminate calcium compounds from the final product, is to calcine first the dolomitic material to form magnesium and calcium oxides which are treated with water to provide an aqueous suspension of magnesium and calcium hydroxides. Such suspension is gassed with carbon dioxide-containing gas, which results in a permanently insoluble precipitate of calcium carbonate, and an initial precipitate of magnesium carbonate. Upon continued gassing, the magnesium carbonate dissolves in the form of magnesium bicarbonate which is water-soluble. In order to effect separation of the calcium carbonate, it is customary commercial practice to gas to the point where substantially all the magnesium is in the form of the water-soluble magnesium bicarbonate, which step enables the calcium carbonate to be removed by filtration.

To obtain magnesium carbonates from the water-soluble magnesium bicarbonate, the magnesium bicarbonate solution is generally heated rapidly to the boiling point, which results in the precipitation of basic magnesium carbonate. If desired, basic magnesium carbonate may be prepared from magnesite in substantially the same manner by calcining the magnesite to form magnesium oxide; treating the magnesium oxide with water to thus form an aqueous suspension of magnesium hydroxide; and gassing such suspension with carbon dioxide-containing gas to form the water-soluble magnesium bicarbonate, which results after initial precipitation of magnesium carbonate. Where dolomitic material is the source of raw material, the magnesium bicarbonate solution will usually contain about 1% to 2% by weight of dissolved magnesia calculated as magnesium bicarbonate. Where magnesite is the raw material, the concentration of magnesium bicarbonate will be slightly higher.

In such prior methods, it was necessary in order to form the magnesium carbonate in blocks or slabs of the desired size or shape, to mold the product under a relatively high mechanical pressure, because the magnesium carbonate did not have self-setting properties or could not undergo a hydraulic set. Thus molding equipment was expensive to maintain and operate as well as to construct. Furthermore, because of the pressure applied during the molding, the product was compacted and consequently made more dense than would occur in a corresponding product having self-setting properties. This, of course, rendered it impractical to intermix with such prior product comparatively large quantities of other heavier materials which might otherwise have been desirable, because the increased density which resulted from such large quantities produced a product having a unit weight too high for commercial specifications. Consequently, the percentages of these foreign materials which could be included was limited.

Our invention has as its objects, among others, the provision of an improved light weight self-setting magnesium carbonate composition having great strength and improved insulating properties, and which can be produced by a comparatively economical process. Other objects of the invention will become apparent from a reading of the following description thereof.

In general, we have discovered that magnesium carbonate having self-setting properties may be formed by decomposition of a magnesium bicarbonate-containing solution. Briefly, such decomposition is effected by excessively agitating a solution containing magnesium bicarbonate, which effects driving off of carbon dioxide, and preferably simultaneously applying a moderate degree of heat to expedite the driving off of the carbon dioxide. This results in the precipitation of fine needle-like normal magnesium carbonate crystals having self-setting properties. Care must be taken to preclude destruction of such normal magnesium carbonate crystals, which would occur should the decomposition reaction be conducted at too high a temperature. Addition of active or caustic magnesium oxide, i. e., magnesium oxide which is not dead burnt, to the magnesium bicarbonate solution is desirable as it has been found to hasten the decomposition reaction. Although such self-setting normal magnesium carbonate crystals are usually formed under most present commercial operating conditions as an intermediate product during the decomposition reaction, their self-setting prop-

erties were not recognized, and they were heretofore destroyed by application of heat at too high a temperature.

If a slurry of such normal magnesium carbonate crystals having self-setting properties is cast or poured into a form or mold, the composition will set in a quiescent state without application of mechanical pressure thereto, to provide the self-setting product of our invention. The setting in the mold is enhanced by application of heat. In other words, we have found that a normal magnesium carbonate in the form of comparatively thin needle-like crystals resulting from the described decomposition of an aqueous magnesium bicarbonate-containing solution, has hydraulic or self-setting properties rendering it unnecessary to mold the composition under pressure to form slabs or blocks. Although the product of our invention has the property of self-setting in a quiescent state without application of pressure thereto, and this is the manner employed by us for producing the product, it will also set if pressure is applied as in other methods heretofore known, and still produce a stronger product than has heretofore been possible by such other methods. Inasmuch as pressure molding is necessary to produce a satisfactory product manufactured by other methods, and in view of the fact that pressure may be applied to the product made by the process of our invention but is not necessary, the expression "independent of pressure" is employed hereinafter to describe that the product of our invention has self-setting properties not conditioned on pressure.

The process of our invention is applicable to any aqueous magnesium bicarbonate-containing solution, irrespective of how such magnesium bicarbonate solution may be prepared. However, it has particular applicability where dolomitic material is employed as the source of raw material and it is desired to remove calcium compounds, because under this condition it is necessary to prepare the magnesium bicarbonate solution in the manner previously related. For all the magnesium to be substantially dissolved in the solution in the form of the bicarbonate, where dolomitic material is the raw material, enough water should be employed to provide a concentration of magnesium of at least about 1% to 2% by weight of the solution, calculated as magnesium bicarbonate. A solution of this strength will be substantially concentrated. However, the process of our invention is applicable to more dilute solutions, as well as to more concentrated solutions which obtain where magnesite is the source of raw material, but obviously if the solutions are too dilute this would be undesirable for commercial reasons because of unnecessary water bulk and the greater cost which would be involved in heating such water.

Vigorous or excessive agitation is important in effecting decomposition of the magnesium bicarbonate, and we have found that the more vigorous the agitation, the more efficacious the decomposition. Mechanical agitation by any suitable agitating mechanism may be employed, but agitation by introducing a stream or streams of compressed air into the vessel in which the reaction occurs is more desirable. Such vessel is preferably open to the atmosphere as the reaction occurs under atmospheric conditions, although it can also be obtained in a vessel maintained under a vacuum, but this is unnecessary. Application of pressure over the vessel would be undesirable because this would interfere with the driving off of carbon dioxide from the magnesium bicarbonate as it decomposes, and thereby impede the decomposition reaction. Agitation has been found to form small and thin crystals which are desirable because the smaller and thinner the crystals, the stronger the final product. This is probably due to the fact that with small thin crystals there is a greater interlacing thereof to provide a firmer bond upon setting of the product.

As was previously related, heat is preferably applied simultaneously with excessive agitation to expedite the decomposition of the magnesium bicarbonate, with consequent precipitation of the normal self-setting magnesium carbonate crystals. However, care must be taken that the temperature is not allowed to rise at any time above the point where the fine needle-like normal magnesium carbonate crystals which are formed lose their character, because then their self-setting properties are destroyed. The temperature should not be permitted to rise much above 120° F.

At present, the process is preferably performed in batches. Live steam introduced directly into the batch provides a suitable heating means and also cooperates to effect agitation. Hence, it is preferred, although any other suitable heating means, such as heating coils in the vessel or external heat, may be employed instead. If some of the normal magnesium carbonate crystals from the first batch are left in the vessel, such crystals serve as a seeding means and expedite formation of succeeding crystals in subsequent batches.

The higher the temperature at which the decomposition is effected, other conditions remaining the same, the more rapid will be the driving off of carbon dioxide from the magnesium bicarbonate. Therefore, it is preferred to conduct the process close to the highest temperature which may be safely employed without impairing the self-setting properties of the crystals. Such temperature, as mentioned above, should not be much over 120° F. At about this temperature, coupled with the vigorous agitation, it will usually take from about one to one and one-half hours to decompose as much as the magnesium bicarbonate as it is commercially practical to decompose from the mother liquor containing such magnesium bicarbonate in solution. This is so because the decomposition of the magnesium bicarbonate is quite rapid during the first half hour of the reaction, and then further decomposition occurs at a decreasingly slower rate. Hence, it would be commercially uneconomical to attempt to decompose all the magnesium bicarbonate at the moderate temperature which should be employed, coupled with vigorous agitation. However, the magnesium bicarbonate which remains in solution in the mother liquor need not be lost, because such mother liquor may be removed from the crystalline magnesium carbonate precipitate and used for treating the original source of magnesium oxide-containing material from which the magnesium bicarbonate solution is to be prepared. Although substantially all of the magnesium bicarbonate could be decomposed by boiling the magnesium bicarbonate solution, this is objectionable for the reasons already explained.

Instead of allowing the decomposition reaction to continue for about one to one and one-half hours, it may be commercially desirable to remove the crystalline normal magnesium carbonate precipitate from the mother liquor after about one-

half hour, which is about the time when the rate of decomposition commences to slow up materially. The operator or observer will be able to determine readily the rate of decomposition of the magnesium bicarbonate as well as how much of the magnesium bicarbonate has been decomposed, by removing at regular intervals successive sample filtrates of the magnesium bicarbonate solution, and titrating such samples with acid, such as sulphuric acid. As the magnesium bicarbonate decomposes, less acid is required to titrate the successive sample filtrates thereof. Suitable amounts of active or caustic magnesium oxide, if desired, may be added to the magnesium bicarbonate solution to aid in the decomposition thereof, to thereby hasten the reaction, but the addition of the magnesium oxide is not necessary.

It is also desirable to take frequent successive samples from the batch as the reaction progresses and make microscopic analyses of the crystals in such samples to insure that proper self-setting crystals are being formed. The proper kind of crystals will appear under the microscope to be substantially all in the form of very fine (not fat), needle-like crystals, ranging from 20 to 50 microns in length and from 2 to 5 microns in thickness. When the decomposition reaction has reached the desirable point for stopping the reaction, agitation and the application of heat are terminated; and the crystals are ready for succeeding steps of the process.

We prefer to add directly to and mix in the reaction vehicle, the usual types of reenforcing materials, such as asbestos fiber, in an amount sufficient to provide a final product which contains from 10% to 15% by weight of the fiber; such product being generally that employed commercially for heat insulation. Other chemically inactive solid bodies, such as vermiculite or diatomaceous earth, may be also mixed in the reaction vehicle. However, such inert filler or reenforcing fiber may be introduced at any suitable subsequent or prior point if so desired.

When the normal magnesium carbonate precipitate is in the form of the desired crystals, and the other material is added to the reaction vehicle, any water-soluble impurities which might be present in the precipitate including magnesium bicarbonate, may be removed by filtration and washing, and the water content of the mass simultaneously adjusted by removal of excess water to control the density of the final set product. A suitable type of filter is an "Oliver" continuous rotary vacuum filter in which removal of excess water, filtration and washing may be done simultaneously. In the particular process herein described, the washing is not necessary if after removal of excess water from the reaction vehicle, in any suitable manner, such as by decantation, any water-soluble magnesium bicarbonate remaining in the slurry, which is undesirable because it has been found to slow up subsequent setting, is neutralized or decomposed completely. For this purpose, we may add sufficient magnesium oxide to the slurry to react with substantially all the magnesium bicarbonate therein to precipitate magnesium carbonate. Lime or any other alkali which will react with water-soluble magnesium bicarbonate to precipitate an insoluble carbonate may be employed instead of the magnesium oxide; the magnesium oxide being preferred to lime because it does not adulterate the product and because it imparts additional strength to the final product. The addition of the neutralizing medium or washing is not necessary but the employment of either one is desirable for the reasons stated.

The resulting normal magnesium carbonate slurry, after separation of the desired amount of water, is now ready to be set. If the resultant slurry is not already markedly alkaline by virtue of the addition thereto of magnesium oxide or equivalent material should washing of the slurry be omitted, we preferably intermix with the slurry to hasten and also control the setting of the product in the molds, and at the same time increase the strength of the final product, an excess of an alkali having the property of consuming carbon dioxide which may be by absorption, adsorption or reaction, such as preferably caustic or active magnesium oxide, an alkali metal hydroxide such as sodium hydroxide, or borax, for a reason to be subsequently explained. Other alkalies, such as lime, may also be employed, but alkalies of this type are not preferred because they cause too much adulteration of the final product. In this connection, enough alkali should be added to render the slurry markedly alkaline, as the slurry has been found to set better when markedly alkaline.

In the setting operation, the slurry is cast or poured directly into forms or molds which are heated for a length of time and at a temperature sufficient to set the slurry or sludge to a firm cake. Agitation of the crystals in the molds is avoided because such agitation will impair the setting of the crystals. Hence, the setting in the molds is accomplished with the crystals in a quiescent state. The composition has substantially no shrinkage on setting and no pressure need be applied to it to accomplish the setting. Consequently, the density of the final product is governed by the quantity of water left in the slurry which is poured into the molds.

During the setting, we have found that carbon dioxide gas is given off; and microscopic observation of the set product shows that the material which was originally all comparatively thin or fine needle-like crystals now consists essentially of a mixture of two crystal forms. Some of the original needle-like crystals remain, but a new very small crystal appears. Such new crystal tends to cluster into grape-like groups, or to adhere to the surface of the needle-like crystals. This probably accounts for the great strength of the final product, which breaks with a clean fracture, in contradistinction to the product of the prior processes, which crushes upon being broken, thus indicating that the product of our invention is bonded by the interlacing of the crystals.

Because of the evolution of the carbon dioxide and the formation of the new crystals, we are led to believe that a reaction probably occurs in which some of the carbonate of magnesium is converted to light basic magnesium carbonate. The carbon dioxide-consuming alkali which is preferably added to the slurry prior to the setting operation, controls and hastens the setting which is preferably conducted in an enclosed chamber, not only because the setting occurs faster when the slurry is made markedly alkaline, but also because the consumption of some of the carbon dioxide reduces the carbon dioxide pressure in such chamber, and thus by the principle of the law of mass action causes the reaction to proceed faster toward the side of the set product.

Also, such alkali since it consumes carbon dioxide, controls the rate of evolution thereof and precludes formation of fissures in the interior of

the setting product which might otherwise result from too rapid an evolution of the carbon dioxide, with consequent weakening of the final product. For any given setting conditions, the length of time of the set may be regulated by the quantity of the carbon dioxide-consuming alkali which may be added to the slurry; the more alkali added within practical limits, the faster being the set. If magnesium oxide alone is added, usually an amount thereof ranging from 1% to 5% by weight of magnesium carbonate, is employed; while borax alone is used in an amount usually ranging from 1% to 2% by weight of magnesium carbonate. An alkali metal hydroxide, such as sodium hydroxide, being much stronger, is employed in lesser quantities; 0.1% to 1% by weight of magnesium carbonate being usually sufficient. Mixtures of the carbon dioxide-consuming alkalies may, of course, be employed if so desired. The addition of the carbon dioxide-consuming alkali, although very desirable for enhancing the set and increasing the strength of the final product, is not essential.

Although no pressure is required to compact or mold the material, pressure molding may be employed and still produce a superior product, or a special dense product for certain purposes. However, such pressure molding is preferably omitted where the final product is intended for heat insulation, inasmuch as it would increase the density. The temperature applied to the molds during setting should not be too high or applied too rapidly, because although the product will set, the evolution of gas is so rapid as to leave the final product with gas holes. Neither should the temperature be too low, because then the setting is, generally speaking, too slow for practical purposes. A suitable temperature range under atmospheric pressure is substantially from 140° F. to 195° F. At this temperature range, the setting to a hard cake will usually occur in from one-half to three hours, the time varying with the temperature actually applied, and also with the chemical and physical character of the composition, as well as the thickness of the mass. Preferably, the setting is effected by placing the slurry filled molds in an enclosure maintained at the desired temperature by live steam, although any other suitable heat may be employed instead. It is desirable that the enclosure in which the setting is conducted be substantially free of drafts to the outside atmosphere because drafts might cause evaporation of moisture and this tends to cause undesirable shrinkage.

The composition sets normally substantially without shrinkage which is important, because if it were to shrink materially, then of course its final shape could not be fixed by the mold, and wasteful trimming would have to be employed to produce the desired shape block or slab. Also, by not shrinking, the density of the product is not increased during the setting thereof, which is important for controlling the final weight of the product, as determined by the amount of water which is in the slurry to be set. In this connection, if the slurry does not have the desired water content to produce the desired density of the final product, water may be added to the slurry in an amount necessary to produce the desired density. Thus, the density of the final product may be controlled by adjusting the water content of the slurry to be set. Under some circumstances, slight shrinkage of the composition might occur during setting, but not as much as the shrinkage which occurs in other commercial processes wherein mechanical pressure molding of the composition is absolutely necessary to produce a satisfactory product.

After having set in molds, the blocks or slabs which are formed are self supporting before they are dry and while containing considerable moisture. Blocks or slabs formed in other commercial processes where the magnesium carbonate is placed in filter molds and pressure molding is employed simultaneously with expulsion of water through perforations in the molds, are not self supporting; and consequently, they have to be supported in frames after they are removed from the molds, so that they will not break during handling prior to drying thereof. The method of our invention, therefore, eliminates the necessity of *having to provide frames to support the molded* product after removal from the molds.

Upon removal of the slabs or blocks from the molds after setting thereof, they are next dried in the usual manner heretofore employed for drying the mechanically molded product. Such drying is accomplished usually in conventional drying ovens at a temperature ranging from 155° F. to 395° F., to remove all uncombined or free water not existing as water of crystallization. Depending on the temperature and draft, it will take from 24 to 72 hours for the drying. The drying, if desired, may be air drying, but oven drying is preferred because it is faster. Should the material tend to stick to the molds upon removal therefrom, the molds may be first greased with any suitable substance such as petroleum grease.

Even though there is substantially no shrinkage of the material in the molds, it may be desirable to mill or trim the surfaces of the dried product so as to provide an attractive product not marred with surface imperfections. Not over 10% of the product need be removed by such milling, whereas with products produced by other methods wherein molding under pressure is required, the amount of product removed by milling runs from 30% to 40%. The milled-off material is not entirely waste material because it may be used for making magnesia insulating cement. However, it has less value as a cement, and therefore results in an economic loss. Hence, because of the lesser amount of material which need be trimmed from the block or slab of our invention, a further economy results. Because the product of our invention sets in a quiescent state substantially without shrinkage, the molds may be made of special shapes so as to form correspondingly shaped insulating fittings.

Standard commercial products of magnesium carbonate insulating blocks produced by former pressure molding methods contain about 85% by weight of magnesium carbonate as a bonding agent and about 15% by weight of asbestos fiber to reenforce the product. Under present standards, such blocks weigh from 16 to 18 lbs. per cubic foot; the specific gravity, therefore, ranging from .25 to .28. The similar product of our invention containing the same percentages of magnesium carbonate and asbestos fiber can be made to weigh as low as 9 lbs. per cubic foot, and will average from 10 to 12 lbs. per cubic foot; the specific gravity, therefore, ranging from .14 to .19. The product of our invention will thus average from 35% to 45% lighter than the corresponding product produced by former methods; and even though lighter, it is much stronger. This comparison between 85% magnesium carbonate blocks of our invention and those heretofore produced holds true for any given specifica-

tion of materials and percentages of magnesium carbonate in the respective blocks. Because of the lightness of the product of our invention, considerable saving in freight charges obtains. Also, due to the low density of our product, it has a lower heat conductivity coefficient than that of products produced by former methods. The heat conductivity coefficient of the product of our invention will run about 20% lower than the corresponding product produced by former methods and containing the same percentages of ingredients.

Although the product of our invention is lighter, it is much stronger than heretofore produced products. Weight for weight, it is 50% to 100% stronger; while a block of our invention, for example an 85% magnesium carbonate block weighing 11 lbs. per cubic foot, will be as strong or even stronger than the corresponding block produced by former methods and averaging 16 to 19 lbs. per cubic foot.

The product of our invention because of its light weight, is highly porous, i. e., cellular in structure, which is one of the factors enabling it to have a high heat insulating efficiency. Furthermore, although the product is shaped, it is not stony or rock-like in character as are artificial stones or natural rocks, but it is chalk-like in character. In other words, compared to an artificial stone or natural rock, it is relatively soft or crushable; the material being readily rubbed off from the surface thereof.

Reference is made to our assignee's copending applications, Serial No. 212,698, filed June 9, 1938, and Serial No. 260,663, filed March 8, 1939, containing related subject matter.

We claim:

1. The method of producing a set magnesium carbonate composition which comprises decomposing magnesium bicarbonate in solution to provide a precipitate of a normal magnesium carbonate in the form of needle-like crystals having self-setting properties, terminating the reaction prior to conversion of said self-setting magnesium carbonate crystals to basic magnesium carbonate so that said self-setting magnesium carbonate crystals form the final precipitate for production of the product to be set, casting a slurry containing such crystals into a form prior to setting thereof, and applying heat to the slurry in the form to enhance setting of such slurry to a firm cake.

2. The method of producing a set magnesium carbonate composition which comprises decomposing magnesium bicarbonate in solution by application of heat and agitation of the solution to provide a precipitate of normal magnesium carbonate in the form of comparatively thin needle-like crystals having self-setting properties independent of application of pressure, controlling the temperature to avoid formation of basic magnesium carbonate with consequent destruction of the self-setting properties of such precipitate, terminating the reaction prior to conversion of said self-setting magnesium carbonate crystals to basic magnesium carbonate so that said self-setting magnesium carbonate crystals form the final precipitate for production of the product to be set, prior to setting thereof casting a slurry containing such crystals into a form adapted to provide the shape of the final product, and applying heat to the slurry in the form to enhance setting of such slurry to a firm cake.

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Patented July 30, 1940 2,209,753

UNITED STATES PATENT OFFICE

2,209,753

MAGNESIUM CARBONATE COMPOSITION AND METHOD OF PREPARATION

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No Drawing. Application June 9, 1938, Serial No. 212,698

3 Claims. (Cl. 23—67)

Our invention relates to magnesium carbonate compositions, and more particularly to an improved magnesium carbonate composition which has the property of self or hydraulically setting with substantially no shrinkage, and also to an improved process for producing such self-setting composition.

Magnesium carbonates are used in sound and heat insulating and similar materials, and have generally comprised either the heavy basic carbonate or the light basic carbonate, or modifications of these materials. These basic carbonates have been prepared by various methods, a common method being that of gassing with carbon dioxide-containing gas an aqueous suspension of magnesium hydroxide to precipitate basic magnesium carbonate. Another type of method is disclosed in the patent to Samuel A. Abrahams, one of the co-applicants of this application, No. 2,027,714, dated January 14, 1936. Briefly, the method of such patent comprises precipitating basic magnesium carbonate from bitterns remaining as residual liquors after crystallization of sodium chloride resulting from the evaporation of sea water, by reaction with an aqueous solution of an alkali metal carbonate, and creating a certain character of precipitate by the application of heat at a temperature between 160° F. and 206° F.

In such prior methods, it was necessary in order to form the magnesium carbonate in blocks or slabs of the desired size and shape, to mold the product in suitable forms under a relatively high mechanical pressure, because the magnesium carbonate did not have self-setting properties or could not undergo a hydraulic set. This molding equipment was expensive to maintain and operate as well as to construct. Furthermore, because of the pressure applied during the molding, the product was compacted and consequently made more dense than would occur in a corresponding product having self-setting properties. This, of course, rendered it impractical to intermix with such prior product comparatively large quantities of other heavier materials which might have been otherwise desirable, because the increased density which resulted from such large quantities produced a product having a unit weight too high for commercial specifications. Consequently, the percentages of these foreign materials which could be included, was limited.

Our invention has as its objects, among others, the provision of an improved light weight self-setting magnesium carbonate composition having great strength and improved insulating properties, and which can be produced by an economical method. Other objects of the invention will become apparent from a reading of the following description thereof.

In general, we have discovered that if the type of process wherein magnesium carbonate is precipitated by reaction of a magnesium compound with a carbonate salt (such as the particular process disclosed in the Abrahams patent mentioned previously), is conducted so as not to destroy the comparatively fine magnesium carbonate needle-like crystals which commence to form shortly after the reaction is initiated and if the reaction is so performed as to leave substantially all the precipitated magnesium carbonate in the form of the fine needle-like crystals, such type of magnesium carbonate crystals, which form normal magnesium carbonate have self-setting properties. Although such self-setting normal magnesium carbonate crystals are always formed by the type of reaction mentioned, their self-setting properties were not recognized, and they were destroyed by subsequent process steps, usually by the application of heat at too high a temperature.

If a slurry of such normal magnesium carbonate crystals having self-setting properties is cast or poured into a form or mold, the composition will set in a quiescent state without application of mechanical pressure thereto, to provide the self-setting product of our invention. The setting in the mold is enhanced by application of heat. In other words, we have found that a normal carbonate of magnesium in the form of comparatively thin needle-like crystals resulting from the described type of reaction, has hydraulic or self-setting properties rendering it unnecessary to mold the composition under pressure to form slabs or blocks. Although the product of our invention has the property of self-setting in a quiescent state without application of pressure thereto, and this is the manner employed by us for producing the product, it will also set if pressure is applied as in other methods heretofore known, and still produce a stronger product than has heretofore been possible by such other methods. Inasmuch as pressure molding is necessary to produce a satisfactory product manufactured by other methods and in view of the fact that pressure may be applied to the product made by the process of our invention but is not necessary, the expression "independent of pressure" is employed hereinafter to describe that the product of our invention has self-setting properties not conditioned on pressure.

In the preferred process of our invention, we economically employ as a source of raw materials for obtaining the desired crystalline magnesium carbonate precipitate, magnesium bittern and a concentrated aqueous sodium carbonate solution which may be made from either soda ash or calcined trona. If trona, which is a natural deposit of sodium carbonate and sodium bicarbonate, is employed, it is preferably calcined to the point where substantially no sodium bicarbonate is left. This is done to minimize as much as possible the formation of water-soluble magnesium bicarbonate because it has been found to slow up setting, and because of its solubility results in loss of magnesium.

These materials may be obtained economically on the Pacific coast; particularly the bittern which occurs as a by-product in the manufacture of salt from sea water, permitted by the climatic conditions on the Pacific coast. The reaction in the beginning is quite similar to that disclosed in the Abrahams patent, stoichiometric quantities of the bittern and the alkali metal carbonate being employed. Although any suitable concentrations of the bittern and the alkali metal carbonate solutions may be employed, we prefer to employ solutions of these substances which are quite concentrated because we have found that the reaction resulting from more concentrated solutions produces a more desirable type of crystal insofar as self-setting properties are concerned.

The reaction is performed in an aqueous vehicle; the total water content preferably being from 10 to 20 parts by weight to one part by weight of the reacting substances. A satisfactory commercial ratio is about 15 or 16 parts of water to one part of the reacting substances. It is undesirable to have too much water because of unnecessary bulk and because, as was previously stated, a more desirable reaction occurs when the water content is relatively low. Too little water obviously impedes the rate of reaction.

Unlike the process in the Abrahams patent, the reaction herein is carried on under vigorous or excessive agitation. Mechanical agitation by any suitable agitating mechanism may be employed, but agitation by introducing a stream or streams of compressed air into the vessel in which the reaction occurs, is more desirable. Such vessel is preferably open to the atmosphere as the reaction occurs under atmospheric conditions, although it can also be obtained in a vessel maintained under pressure or vacuum but this is unnecessary. Agitation has been found to form small and thin crystals which are desirable because the smaller and thinner the crystals, the stronger the final product. This is probably due to the fact that with small thin crystals there is a greater interlacing thereof to provide a firmer bond upon setting of the product.

The process is at present perferably performed in batches. When the first reaction bath is started, it is desirable to heat the batch as this has been found to facilitate and hasten the reaction. However, care must be taken that the temperature of the bath is not allowed to rise at any time above the point where the fine needle-like normal magnesium carbonate crystals which are formed, lose their character because then their self-setting properties are destroyed. The temperature should not be permitted to rise much over 120° F., and preferably, the temperature should be maintained between 75° F. and 90° F. In the process of the Abrahams patent referred to, the self-setting magnesium carbonate crystals are destroyed by the high temperature applied during the later steps of the process.

Live steam introduced directly into the batch provides a suitable heating means and also cooperates to effect agitation. Hence, it is preferred, although any other suitable heating means, such as heating coils in the vessel or external heat, may be employed instead. If some of the magnesium carbonate crystals from the first batch are left in the vessel, such crystals serve as a seeding means and expedite formation of succeeding crystals, thus shortening the time of reaction which is advantageous from the viewpoint of commercial economy.

The magnesium carbonate crystals may also be obtained by the reaction of any other magnesium compound and any other water-soluble carbonate which are known upon reaction to precipitate substantially water-insoluble magnesium carbonate. For example, Epsom salts or magnesium containing brines found in wells, and any other water-soluble carbonate, such as any of the alkali metal carbonates, can be employed.

When the reaction first commences, the batch has a comparatively thin consistency, but as the reaction proceeds and the fine needle-like self-setting magnesium carbonate crystals begin to form, the batch thickens. A skilled operator or observer will be able to determine when substantially all of the magnesium carbonate is in the form of the desired self-setting magnesium carbonate crystals, because when such point occurs, the batch has a maximum thickness, being almost gelatinous in character, and then immediately starts to thin out. This is the way by which the operator can tell when the reaction is at the proper end point.

However, the most accurate and preferred way to ascertain the proper end point of the reaction is by taking frequent successive samples from the batch as the reaction proceeds and making microscopic analyses of the crystals in such samples. At first, when the reaction has just been initiated by intermixing of the reacting substances, the precipitate is not in the form of needle-like normal magnesium carbonate crystals, but appears under the microscope more in the form of amorphous grape-like clusters. The fine needle-like crystals form as the reaction continues; and successive early samples thereof show more and more of such crystals.

When the reaction is at the desired end point, substantially all of the magnesium carbonate precipitate appears under the microscope to be in the form of very fine (not fat) needle-like crystals, ranging from 20 to 50 microns in length, and from 2 to 5 microns in thickness. At such end point, agitation, and the application of heat if applied, are terminated; and the crystals are ready for succeeding steps of the process. The length of time for the reaction to be completed in the first batch which is heated, although not critical, is usually from 20 minutes to ½ hour. For succeeding batches in which the crystals are formed by seeding in the manner explained above, the reaction is much faster.

By virtue of the presence of small quantities of sodium bicarbonate sometimes occurring in commercial sources of the sodium carbonate or calcined trona, a small amount of water-soluble magnesium bicarbonate is formed in the reaction vehicle, which has been found to slow up the subsequent setting, as was previously mentioned. To neutralize any small amount of water-soluble magnesium bicarbonate which

might be formed in the reaction vehicle and thereby preclude it from slowing up the setting of the magnesium carbonate crystals, should all the bicarbonate be not washed away from such crystals during a washing operation to be subsequently described, we may add to the reaction vehicle a quantity of caustic or active magnesium oxide, i. e., magnesium oxide which is not dead burnt, sufficient to react with all the water-soluble magnesium bicarbonate to precipitate magnesium carbonate. This also increases the yield. Lime, or any other alkali which will react with water-soluble magnesium bicarbonate to precipitate an insoluble carbonate, may be employed instead of the magnesium oxide; the magnesium oxide being preferred to lime, because it does not adulterate the product and because it imparts additional strength to the final set product. The addition of the neutralizing medium is not necessary, but its employment may be desirable for the reasons stated.

We prefer to add directly to and mix in the reaction vehicle, the usual types of reenforcing materials, such as asbestos fiber, in an amount sufficient to provide a final product which contains from 10% to 15% by weight of the fiber; such product being generally that employed commercially for heat insulation. Other chemically inactive solid bodies, such as vermiculite or diatomaceous earth, may be also mixed in the reaction vehicle. However, such inert filler or reenforcing fiber may be introduced at any suitable subsequent or prior point if so desired.

As soon as the end point of the reaction is reached, namely when substantially all of the normal magnesium carbonate precipitate is in the form of the desired crystals, and the other material is added to the reaction vehicle, water-soluble impurities including magnesium bicarbonate are removed preferably by filtration and washing, and the water content of the mass is simultaneously adjusted by removal of excess water to control the density of the final set product. A suitable type of filter is an "Oliver" continuous rotary vacuum filter in which removal of excess water, filtration and washing may be done simultaneously.

The resulting magnesium carbonate slurry, after washing and separation of the desired amount of water, is now ready to be set. If the resultant slurry is not already markedly alkaline by virtue of the addition of magnesium oxide or equivalent material to the reaction vehicle, we preferably intermix with the slurry to hasten and also control the setting of the product in the molds, and at the same time increase the strength of the final product, an excess of an alkali having the property of consuming carbon dioxide which may be by absorption, adsorption or reaction, such as preferably caustic or active magnesium oxide, an alkali metal hydroxide such as sodium hydroxide, or borax for a reason to be subsequently explained. Other alkalies, such as lime, may also be employed, but alkalies of this type are not preferred because they cause too much adulteration of the final product. In this connection, enough alkali should be added to render the slurry markedly alkaline, as the slurry has been found to set better when markedly alkaline.

In the setting operation, the slurry is cast or poured directly into forms or molds which are heated for a length of time and at a temperature sufficient to set the slurry or sludge to a firm cake. Agitation of the crystals in the molds is avoided because such agitation will impair the setting of the crystals. Hence, the setting in the molds is accomplished with the crystals in a quiescent state. The composition has substantially no shrinkage on setting and no pressure need be applied to it to accomplish the setting. Consequently, the density of the final product is governed by the quantity of water left in the slurry which is poured into the molds.

During the setting, we have found that carbon dioxide gas is given off; and microscopic observation of the set product shows that the material which was originally all comparatively thin or fine needle-like crystals now consists essentially of a mixture of two crystal forms. Some of the original needle-like crystals remain but a new, very small crystal appears. Such new crystal tends to cluster into grape-like groups, or to adhere to the surface of the needle-like crystals. This probably accounts for the great strength of the final product, which breaks with a clean fracture, in contradistinction to the product of the prior processes, which mushes upon being broken, thus indicating that the product of our invention is bonded by the interlacing of the crystals.

Because of the evolution of the carbon dioxide and the formation of the new crystals, we are led to believe that a reaction probably occurs in which some of the normal carbonate of magnesium is converted to light basic magnesium carbonate. The carbon dioxide-consuming alkali which is preferably added to the slurry prior to the setting operation, controls and hastens the setting which is preferably conducted in an enclosed chamber, not only because the setting occurs faster when the slurry is made markedly alkaline, but also because the consumption of some of the carbon dioxide reduces the carbon dioxide pressure in such chamber, and thus by the principle of the law of mass action causes the reaction to proceed faster toward the side of the set product. Also, such alkali since it consumes carbon dioxide, controls the rate of evolution thereof and precludes formation of fissures in the interior of the setting product, which might otherwise result from too rapid an evolution of the carbon dioxide, with consequent weakening of the final product. For any given setting conditions, the length of time of the set may be regulated by the quantity of the carbon dioxide consuming alkali which may be added to the slurry; the more alkali added within practical limits, the faster being the set. If magnesium oxide alone is added, usually an amount thereof ranging from 1% to 5% by weight of magnesium carbonate, is employed; while borax alone is used in an amount usually ranging from 1% to 2% by weight of magnesium carbonate. An alkali metal hydroxide, such as sodium hydroxide, being much stronger, is employed in lesser quantities; 0.1% to 1% by weight of magnesium carbonate being usually sufficient. Mixtures of the carbon dioxide-consuming alkalies may, of course, be employed if so desired. The addition of the carbon dioxide-consuming alkali, although very desirable for enhancing the set and increasing the strength of the final product, is not essential.

Although no pressure is required to compact or mold the material, pressure molding may be employed and still produce a superior product, or a special dense product for certain purposes. However, such pressure molding is preferably omitted where the final product is intended for

heat insulation, inasmuch as it would increase the density. The temperature applied to the molds during setting should not be too high or applied too rapidly, because although the product will set, the evolution of gas is so rapid as to leave the final product with gas holes. Neither should the temperature be too low, because then the setting is, generally speaking, too slow for practical purposes. A suitable temperature range under atmospheric pressure is substantially from 140° F. to 195° F. At this temperature range, the setting to a hard cake will usually occur in from ½ to 3 hours, the time varying with the temperature actually applied, and also with the chemical and physical character of the composition, as well as the thickness of the mass. Preferably, the setting is effected by placing the slurry filled molds in an enclosure maintained at the desired temperature by live steam, although any other suitable heat may be employed instead. It is desirable that the enclosure in which the setting is conducted be substantially free of drafts to the outside atmosphere because drafts might cause evaporation of moisture and this tends to cause undesirable shrinkage.

The composition sets normally substantially without shrinkage which is important, because if it were to shrink materially, then of course its final shape could not be fixed by the mold, and wasteful trimming would have to be employed to produce the desired shape block or slab. Also, by not shrinking, the density of the product is not increased during the setting thereof, which is important for controlling the final weight of the product, as determined by the amount of water which is in the slurry to be set. In this connection, after the previously described filtering and washing of the slurry, if it does not have the desired water content to produce the desired density of the final product, water may be added to the slurry in an amount necessary to produce the desired density. Thus, the density of the final product may be controlled by adjusting the water content of the slurry to be set. Under some circumstances, slight shrinkage of the composition might occur during setting, but not as much as the shrinkage which occurs in other commercial processes wherein mechanical pressure molding of the composition is absolutely necessary to produce a satisfactory product.

After having set in molds, the blocks or slabs which are formed are self-supporting before they are dry and while containing considerable moisture. Blocks or slabs formed in other commercial processes where the magnesium carbonate is placed in filter molds and pressure molding is employed simultaneously with expulsion of water through perforations in the molds, are not self-supporting; and consequently they have to be supported in frames after they are removed from the molds, so that they will not break during handling prior to drying thereof. The method of our invention, therefore, eliminates the necessity of having to provide frames to support the molded products after removal from the molds.

Upon removal of the slabs or blocks from the molds after setting thereof, they are next dried in the usual manner heretofore employed for drying the mechanically molded product. Such drying is accomplished usually in conventional drying ovens at a temperature ranging from 135° F. to 395° F., to remove all uncombined or free water not existing as water of crystallization. Depending on the temperature and draft, it will take from 24 to 72 hours for the drying. The drying, if desired, may be air drying, but oven drying is preferred because it is faster. Should the material tend to stick in the molds upon removal therefrom, the molds may be first greased with any suitable substance such as petroleum grease.

Even though there is substantially no shrinkage of the material in the molds, it may be desirable to mill or trim the surfaces of the dried product so as to provide an attractive product not marred with surface imperfections. Not over 10% of the product need be removed by such milling, whereas with products produced by other methods wherein molding under pressure is required, the amount of product removed by milling runs from 30% to 40%. The milled-off material is not entirely waste material because it may be used for making magnesia insulating cement. However, it has less value as a cement, and therefore results in an economic loss. Hence, because of the lesser amount of material which need be trimmed from the block or slab of our invention, a further economy results. Because the product of our invention sets in a quiescent state substantially without shrinkage, the molds may be made of special shapes so as to form correspondingly shaped insulating fittings.

Standard commercial products of magnesium carbonate insulating blocks produced by former pressure molding methods contain about 85% by weight of magnesium carbonate as a bonding agent and about 15% by weight of asbestos fiber to reenforce the product. Under present standards, such blocks weigh from 16 to 18 lbs. per cubic foot; the specific gravity, therefore ranging from .25 to .28. The similar product of our invention containing the same percentages of magnesium carbonate and asbestos fiber can be made to weigh as low as 9 lbs. per cubic foot, and will average from 10 to 12 lbs. per cubic foot; the specific gravity, therefore, ranging from .14 to .19. The product of our invention will, thus, average from 35% to 45% lighter than the corresponding product produced by former methods; and even though lighter, it is much stronger. This comparison between 85% magnesium carbonate blocks of our invention and those heretofore produced holds true for any given specification of materials and percentages of magnesium carbonate in the respective blocks. Because of the lightness of the product of our invention, considerable saving in freight charges obtains. Also, due to the low density of our product, it has a lower heat conductivity coefficient than that of products produced by former methods. The heat conductivity coefficient of the product of our invention will run about 20% lower than the corresponding product produced by former methods and containing the same percentages of ingredients.

Although the product of our invention is lighter, it is much stronger than heretofore produced products. Weight for weight, it is 50% to 100% stronger; while a block of our invention, for example an 85% magnesium carbonate block weighing 11 lbs. per cubic foot, will be as strong or even stronger than the corresponding block produced by former methods and averaging 16 to 18 lbs. per cubic foot.

The product of our invention because of its light weight, is highly porous, i. e., cellular in structure, which is one of the factors enabling it to have a high heat insulating efficiency. Furthermore, although the product is shaped, it is not stony or rock-like in character as are artificial stones or natural rocks, but it is chalk-like in character. In

other words, compared to an artificial stone or natural rock, it is relatively soft or crushable; the material being readily rubbed off from the surface thereof.

Reference is made to our assignee's copending applications, Serial No. 212,696, filed June 9, 1938, and Serial No. 260,653 filed March 8, 1939, containing related subject matter.

We claim:

1. The method of producing a set magnesium carbonate composition which comprises effecting a reaction between a magnesium compound and a metallic carbonate salt to precipitate normal magnesium carbonate in the form of needle-like crystals having self-setting properties, terminating the reaction prior to conversion of said self-setting magnesium carbonate crystals to basic magnesium carbonate so that said self-setting magnesium carbonate crystals form the final precipitate for production of the product to be set, casting a slurry containing such crystals into a form prior to setting thereof, and applying heat to the slurry in the form to enhance setting of such slurry to a firm cake.

2. The method of producing a set magnesium carbonate composition which comprises effecting a reaction in an aqueous vehicle under conditions of heat and agitation between a magnesium compound and a water soluble metallic carbonate salt to precipitate normal magnesium carbonate in the form of comparatively thin needle-like crystals having self-setting properties independent of application of pressure, controlling the temperature to avoid destruction of the self-setting properties of such precipitate, terminating the reaction prior to conversion of said self-setting magnesium carbonate crystals to basic magnesium carbonate, casting a slurry containing said self-setting magnesium carbonate crystals into a form prior to setting thereof, applying heat to the slurry in the form to enhance setting of the slurry to a firm cake, and subsequently drying the resultant cake.

3. The method of producing a set magnesium carbonate composition which comprises effecting a reaction in an aqueous vehicle under conditions of heat and agitation between magnesium bittern and a water soluble metallic carbonate salt to precipitate normal magnesium carbonate in the form of comparatively thin needle-like crystals having self-setting properties independent of application of pressure, controlling the temperature to avoid destruction of the self-setting properties of such precipitate, terminating the reaction prior to conversion of said self-setting magnesium carbonate crystals to basic magnesium carbonate, washing said self-setting magnesium carbonate crystals substantially free of impurities, casting a slurry containing said self-setting magnesium carbonate crystals into a form prior to setting thereof, applying heat to the slurry in the form to enhance setting of the slurry to a firm cake, and subsequently drying the resultant cake.

SAMUEL A. ABRAHAMS.
RUBIN LEWON.

CERTIFICATE OF CORRECTION.

Patent No. 2,209,758. July 30, 1940.

SAMUEL A. ABRAHAMS, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 5, first column, line 22, claim 1, for the word "settling" read --setting--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of September, A. D. 1940.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

Patented July 30, 1940 2,209,754

UNITED STATES PATENT OFFICE

2,209,754

SELF-SET MAGNESIUM CARBONATE COMPOSITION AND METHOD OF EFFECTING SETTING THEREOF

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No Drawing. Application March 8, 1939, Serial No. 260,663

18 Claims. (Cl. 18—48)

Our invention relates to magnesium carbonate compositions, and more particularly to an improved method for effecting setting of a slurry containing magnesium carbonate prepared to possess self-setting properties and to an improved final product. This application is a continuation in part of our co-pending application, Serial No. 212,697, filed June 6, 1938.

In our assignee's co-pending application, Serial No. 2112,698, filed June 9, 1938, we have disclosed a type of method whereby such self-setting magnesium carbonate may be prepared. Briefly, such type of method comprises precipitating comparatively fine needle-like magnesium carbonate crystals in an aqueous vehicle by reaction of a magnesium compound, such as sea water bittern, with a carbonate salt, such as sodium carbonate. In this crystalline form, the magnesium carbonate possesses self-setting properties. Care is taken during the reaction to prevent total or partial destruction of such crystals after they form, which destruction would occur should the reaction be conducted at too high a temperature, resulting in loss or impairment of their self-setting properties. Excessive agitation during the reaction has been found to expedite the formation of such crystals, and is consequently employed. The magnesium carbonate crystals having most desirable self-setting properties for subsequent employment in the manufacture of insulating products, when examined under the microscope, will usually range from about twenty (20) to fifty (50) microns in length and from about two (2) to five (5) microns in thickness.

Our assignee's co-pending application, Serial No. 212,696, filed June 9, 1938, discloses another type of method whereby the described self-setting magnesium carbonate crystals may be obtained by decomposition of an aqueous solution of magnesium bicarbonate. Briefly, such decomposition is effected by excessively agitating the magnesium bicarbonate solution and simultaneously applying heat, to thus drive off carbon dioxide, which results in the precipitation of the self-setting magnesium carbonate crystals. Care is also taken during formation of the crystals to preclude total or partial destruction thereof by too high a temperature. Addition of active or caustic magnesium oxide to the magnesium bicarbonate solution, has been found to hasten the decomposition reaction.

Such self-setting magnesium carbonate crystals may be also formed by passing with carbon dioxide-containing gas an aqueous vehicle containing a suspension of magnesium hydroxide. In commercial practice, the magnesium hydroxide suspension is generally formed by treating with water calcined magnesite (a natural occurring magnesium carbonate) or calcined dolomitic material (a natural occurring mineral composed essentially of calcium carbonate and magnesium carbonate). In such method, the precipitation of the self-setting carbonate of magnesium crystals occurs as the gassing with carbon dioxide-containing gas proceeds.

Care should be taken that the temperature of the reaction does not get too high because if it does the self-setting properties of the magnesium carbonate crystals would be impaired, if not destroyed. For best results, the reaction should also be controlled to convert substantially all of the magnesium ions in the reacting medium to the described crystalline carbonate of magnesium, as the presence of magnesium in a form other than the fine needle-like crystals impairs the setting properties of the product. As with respect to the formation of such magnesium carbonate crystals by reaction of a magnesium compound with a carbonate salt in an aqueous vehicle, and by the decomposition of a magnesium bicarbonate solution, excessive agitation will enhance the formation thereof in the gassing method.

A suitable temperature range for conducting the gassing method is between sixty-eight degrees Fahrenheit (68° F.) and one hundred four degrees Fahrenheit (104° F.), preferably at about eighty-six degrees Fahrenheit (86° F.); the quantity of water being preferably from fifteen (15) parts to as high as sixty (60) parts per part of magnesium oxide, by weight.

In the case where dolomitic material is used as a source of raw material, the inherent lightness of the final product resulting from the self-setting properties thereof, enables a slurry containing both the calcium carbonate which is insoluble and the self-setting magnesium carbonate crystals, to be set as such. In other words, the calcium carbonate need not be removed for the production of a satisfactory light weight heat insulating block, as is required in other commercial pressure molding processes where dolomitic material is the source of raw material.

From the preceding, it is seen that at some point during the preparation of a carbonate of magnesium by a reaction, in an aqueous reaction vehicle, which consists essentially of the combination of magnesium and carbonate ions, a precipitate of comparatively fine or thin needle-

like crystals of magnesium carbonate is formed; and this crystalline magnesium carbonate which is a normal hydrated magnesium carbonate, believed to be the trihydrate, has self-setting properties. In this connection, it is desirable to obtain relatively small needle-like crystals because these have been found to provide greater strength in the final product than that obtainable by larger crystals. Excessive agitation will produce the desirable smaller crystals which for most desirable self-setting properties for subsequent employment in the manufacture of insulating products, will usually range from about twenty (20) to fifty (50) microns in length and from about two (2) to five (5) microns in thickness, as was previously mentioned.

If a slurry of such normal hydrated magnesium carbonate crystals is cast or poured into a form or mold, the composition will set in a quiescent state to provide a self-set final product; the setting in the mold being materially expedited by application of heat. The composition has substantially no shrinkage upon setting; and no mechanical pressure need be applied thereto, as is necessary in other methods, wherein the magnesium carbonate is usually molded under mechanical pressure in a filter mold, simultaneously with the expulsion of water therefrom through perforations in such filter mold. As a result, the density of the self-set product may be governed by the quantity of water left in the slurry which is poured into the mold, and such mold need not be perforated.

The usual types of reenforcing materials, such as asbestos or other suitable reenforcing fiber, in an amount sufficient to provide a final product which contains from ten percent. (10%) to fifteen percent. (15%) by weight of the fiber, may be intermixed with the slurry to be set; such product being generally that employed commercially for heat insulating purposes. Other chemically inactive solid bodies, such as vermiculite or diatomaceous earth, may be also mixed in the slurry. Such inert filler or reenforcing fiber may be mixed directly in the slurry after it is formed, or if desired, they may be incorporated in the reaction vehicle in which the self-setting magnesium carbonate crystals are formed.

We have found that certain conditions of alkalinity of the slurry will enable control of the setting and also permit such setting to occur more expeditiously as well as impart increased strength to the final product; and, if the setting is conducted under special controlled conditions, a superior grade product will result. Also, we have found that the slurry before being cast into a form or mold wherein it is to be set, may be preheated to cooperate in hastening the time of setting in the form. Our invention, therefore, has as its objects, among others, the provision of improvements in the product and in the manner of obtaining setting of the described self-setting magnesium carbonate crystals. Other objects of the invention will become apparent from a perusal of the following description thereof.

In general, we have found that if the slurry of the magnesium carbonate crystals to be set is not already markedly alkaline (i. e. alkaline reserve sufficient to neutralize magnesium bicarbonate generally present in the slurry and consume some of the carbon dioxide which is given off during the setting), the addition of a carbon dioxide consuming alkali thereto in a quantity sufficient to render the slurry markedly alkaline, will provide a control for the setting of the product and allow such setting to be expedited; and in addition impart added strength to the final product. To further expedite setting in the form, the slurry may be preheated prior to being cast therein. Also, we have found that the setting is best conducted in an environment wherein substantially no drying or dehydration of the setting mass can occur; so that there is very little, if any, loss in weight thereof. This helps to preclude any shrinkage which might tend to occur. Drying of the set product is effected by a separate and independent subsequent step. With respect to forms wherein a comparatively large surface area of the setting mass is exposed so that moisture can readily evaporate from such exposed area, such as open pans, the setting to accomplish the best results should be in an enclosed chamber substantially free of drafts to the outside atmosphere and which is moisture-laden to the point where the atmosphere under which the setting occurs is substantially moisture-saturated with respect to the vapor pressure of the water in the mass being set, to preclude evaporation of moisture from the setting mass. The same effect may be obtained in an open space when forms are employed which enclose substantially all of the surface area of the setting mass, such as a tube-like form in which the setting mass is exposed only at an end of the form. In this event, substantially no moisture can evaporate during the setting period, and such forms, therefore, provide the means for precluding drying or dehydration of the setting mass. Steam can be employed as the source of heat when forms of the latter type are utilized but any other suitable heat may be employed if desired.

Although all the steps of heating the slurry before it is cast into the form, utilizing a markedly alkaline slurry, and conducting the setting in an environment wherein drying of the setting mass is precluded, are employed, the step of utilizing a markedly alkaline slurry may be omitted, and still produce a satisfactory product. Also, the step of setting the slurry without substantial dehydration in a substantially non-drying atmosphere, may be omitted, and still produce a good product. The step of preheating the slurry prior to pouring it into the forms is desirable because it enables the setting to be conducted in a shorter time, thereby making for economy of manufacture. However, such step may be omitted without effecting the quality of the final product. For the production of a superior product, the setting should be conducted under the described conditions wherein substantially no drying of the setting mass can occur and the slurry is rendered markedly alkaline. In addition to effecting the quality of the final product, the markedly alkaline slurry, as previously pointed out, permits expedition of the setting. Therefore, the combination of this step and the preheating step are important in obtaining a fast set.

Our improved method of setting the slurry containing the described self-setting needle-like magnesium carbonate crystals will now be described in greater detail. Such magnesium carbonate is a normal hydrated magnesium carbonate, believed to be the trihydrate, which sets by conversion to a basic magnesium carbonate, the conversion being enhanced by application of heat. Heretofore, it was deemed necessary to avoid application of heat to the mag-

nesium carbonate crystals during the period between the termination of the reaction by which they are formed and prior to the setting thereof in the forms or molds. We have now found that heat may be applied during this period without weakening the final set of the product in the molds, provided the temperature and time are below the critical point at which the normal carbonate commences to undergo conversion to a basic carbonate. If the preheating temperature is too high, such conversion will occur in a relatively short time, while if the temperature is low but applied over a relatively long time, the conversion will also occur. The skilled operator can readily ascertain when such conversion commences because when it does the slurry starts to thicken or gel. Any preheating of the slurry before it is poured into the forms should, therefore, be below the point at which incipient conversion or gelling occurs.

Preheating of the slurry after it is formed and before being poured into the molds is desirable for commercial reasons because it enables the setting time to be materially shortened in the molds, thus resulting in economy of manufacture. The preheating should be conducted to bring all of the slurry to a substantially uniform temperature as quickly as possible before pouring into the molds. This can be best accomplished by heating relatively small batches of the slurry, and simultaneously stirring or mixing such batches to provide the uniform incorporation of the heat. The preheating may be conducted in open heated vessels if so desired; or by conveying the slurry through heated screw conveyors which serve to mix the slurry as well as convey it. Although conversion of the slurry to a basic magnesium carbonate will occur at widely varying temperatures, depending on the character of the self-settable normal magnesium carbonate crystals, we have found that in most cases such conversion occurs readily at a temperature of about one hundred thirty degrees Fahrenheit (130° F.) to one hundred seventy degrees Fahrenheit (170° F.). It is generally desirable to employ masses being preheated which take about ten (10) to fifteen (15) minutes to bring all of the slurry up to the desired preheating temperature. It is undesirable to have conversion from the self-settable normal hydrated magnesium carbonate crystals to a basic magnesium carbonate occur during the preheating because the entire setting should occur in the molds to provide a final product of maximum strength. As was previously pointed out, the preheating step may be omitted, if so desired.

To hasten and also control the setting of the slurry containing such crystals whether it is or is not preheated, and at the same time increase the strength of the final product, we preferably render it markedly alkaline, if it is not already markedly alkaline, by adding thereto either prior to or after preheating if employed, or to the vehicle from which it is formed, an excess of an alkali having the property of consuming carbon dioxide which may be by absorption, adsorption or reaction, such as preferably caustic or active magnesium oxide, i. e., magnesium oxide which is not dead burnt, borax, or an alkali metal hydroxide such as sodium hydroxide, or any suitable mixtures thereof. An alkali, such as lime, may also be employed, but is not desirable because it would adulterate the final product to too great an extent. The carbon dioxide-consuming alkali which is added to the slurry prior to the setting is believed to enter into a reaction with other substances existing in the setting slurry. For any given setting conditions, the length of time of the set may be regulated by the quantity of the carbon dioxide-consuming alkali which may be added to the slurry; the more alkali added within practical limits, the faster being the set permitted. In this connection, the carbon dioxide-consuming alkali also permits faster setting than would otherwise be permitted with respect to any given slurry which does not have the carbon dioxide-consuming alkali therein because it allows the setting to be conducted at higher temperatures, to thereby hasten the conversion to a basic carbonate.

If only magnesium oxide is added, usually an amount thereof ranging from one percent. (1%) to ten percent. (10%) by weight of magnesium carbonate in the slurry will suffice. Borax, being a stronger alkali, is added in an amount ranging from one percent. (1%) to two percent. (2%) by weight of magnesium carbonate. An alkali metal hydroxide, such as sodium hydroxide, being still stronger, is employed in an amount ranging from one-tenth of one percent. (0.1%) to one percent. (1%) by weight of magnesium carbonate in the slurry. Magnesium oxide has the advantage of not adulterating the product at all, and, therefore, provides for greatest added strength. The stronger alkalies, such as borax and sodium hydroxide, however, permit faster setting. Therefore, a mixture of magnesium oxide and borax or an alkali metal hydroxide, produces ideal results. Such mixture may contain these substances in any desirable proportions.

The upper limit of the amount of alkali which should be added is not particularly critical, as the maximum quantity may be determined at the time by one skilled in the art, in accordance with the conditions. It is only important that the slurry be made markedly alkaline, that is, sufficiently alkaline to neutralize any magnesium bicarbonate present, which has the unfortunate property of inhibiting the set and is consequently undesirable, and provide a reserve to consume some of the carbon dioxide which is evolved during setting. In the setting operation, the slurry is cast or poured directly into imperforate forms or molds which are heated for a length of time and at a temperature sufficient to set the slurry or sludge to a firm cake. Agitation of the self-setting magnesium carbonate crystals in the mold is avoided because such agitation will impair the setting of the product. Hence, the setting in the mold is accomplished with the crystals in a quiescent state. As was previously related, the composition sets with substantially no shrinkage and no pressure need be applied to it to accomplish the setting. As a result, the density of the final product is governed by the quantity of water left in the slurry which is poured into the mold. It is to be understood that the self-settable normal hydrated magnesium carbonate crystalline precipitate is not allowed to set in the reaction vehicle and that such reaction vehicle usually contains an excess of water, a desired amount of which is usually removed, in any suitable way such as by decantation or filtration, to determine the density of the final product. More water than desired is usually removed when the precipitate is separated from the reaction vehicle, for example for the purpose of washing it, but additional water

may be added afterwards to provide a final product of the desired density.

During the setting, we have found that carbon dioxide gas is given off; and microscopic observation of the set product shows that the magnesium carbonate which was originally all comparatively thin or fine needle-like crystals now consists essentially of a new crystal form. Some of the original needle-like crystals may remain, but a new, very small crystal appears. Such new crystal tends to cluster into grape-like groups, or to adhere to the surface of the needle-like crystals. This probably accounts for the great strength of the final product which breaks with a clean fracture, in contradistinction to the product of the prior processes wherein pressure molding is employed, which mushes upon being broken, thus indicating that the product of our invention is bonded by the interlacing of the crystals.

Because of the evolution of the carbon dioxide gas and the formation of the new crystals, a reaction occurs in which the carbonate of magnesium is converted into a light basic magnesium carbonate. The carbon dioxide-consuming alkali which is preferably added to the slurry prior to the setting operation, allows hastening and control of the setting which is preferably conducted in an enclosed chamber when the molds are of such character as to expose a relatively large surface area of the setting mass, such as open pans, not only because the setting can occur faster when the slurry is made markedly alkaline, but also because the consumption of some of the carbon dioxide reduces the carbon dioxide pressure in such setting mass, and thus by the principle of the law of mass action, causes the reaction to proceed faster toward the side of the set product. Also, such alkali since it consumes carbon dioxide, controls the rate of evolution thereof and precludes formation of fissures in the interior of the setting product, which might otherwise result from too rapid an evolution of the carbon dioxide, with consequent weakening of the final product.

Although no pressure is required to compact or mold the material, since the material sets in a quiescent state independent of pressure, pressure molding may be employed and still produce a superior product, or a special dense product for certain purposes. However, such pressure molding is preferably omitted inasmuch as it would increase the density of the final product, which is undesirable where the product is to be employed for heat insulating purposes. Inasmuch as pressure molding has heretofore been necessary because the magnesium carbonate produced by other methods does not have self-setting properties, and because pressure may be applied to the self-settable magnesium carbonate of our invention but is not necessary, the expression "independent of pressure" is employed hereinafter to describe that the magnesium carbonate of our invention has self-setting properties not conditioned on pressure.

When preheating of the slurry is not employed and the molds are of such character as to expose a relatively large surface area of the setting mass, the temperature applied to the molds during the setting should not be too high or applied too rapidly, because, although the product will set, the evolution of gas may be so rapid as to leave the final product with gas holes. Neither should the temperature be too low, because then the setting is, generally speaking, too slow for practical purposes. A suitable temperature range under atmospheric pressure is substantially from one hundred forty degrees Fahrenheit (140° F.) to one hundred ninety-five degrees Fahrenheit (195° F.). At this temperature range, the setting to a hard cake in molds which expose a relatively large surface area of the product will usually occur in from one-half to three (½ to 3) hours, the time varying, of course, with the temperature actually applied, and also with the chemical and physical character of the composition, as well as the thickness of the mass. If the slurry is preheated, and also markedly alkaline, the setting in molds which expose a relatively large surface area of the product, can be accomplished in about three to fifteen (3 to 15) minutes at a lower temperature of about one hundred thirty degrees Fahrenheit (130° F.) to one hundred seventy degrees Fahrenheit (170° F.)

For best results, it is important that the setting be conducted so that substantially no drying or dehydration of the composition occurs during the setting thereof, as this minimizes shrinkage should the setting product have any tendency to shrink. For this reason, we effect the setting in our improved method when the product is cast into molds which expose a relatively large surface area of the product, by placing the slurry-filled molds in an enclosure or chamber maintained at the desired temperature by live moist steam introduced therein under pressure. Furthermore, it is important that the enclosure in which the setting is conducted be free of any substantial drafts to the outside atmosphere because drafts might cause carrying of moisture from the product as it sets, and this might cause undesirable drying which might result in shrinkage. By employing live steam as the heating medium for effecting the setting in the molds, the region or atmosphere in which the setting occurs can be made moisture-saturated or oversaturated with respect to the vapor pressure of the water in the setting material, to thereby minimize evaporation of moisture therefrom and avoid shrinkage. Under the prescribed setting conditions, the slurry after it has set in the mold and before it is dried by a subsequent drying step to be described, will weigh substantially the same as it did when first cast into the mold.

Instead of live steam as a source of heat, the same effect may be obtained by using an external source of heat to heat the chamber in which the setting is conducted, and by introducing a spray or other source of water into the chamber to render the atmosphere therein moisture-laden. However, steam is preferred because it penetrates the setting mass to thereby replace more readily any moisture which might tend to be driven off because of the heat. If molds are employed which substantially completely jacket the slurry, such as a tube-like mold wherein the slurry is only exposed at an end of the mold, then such type of mold serves by itself to preclude substantial evaporation of moisture during the setting, and causes the setting to occur under non-drying conditions. Although steam heat may be employed for heating such form or mold, it is not necessary, as any other suitable kind of heat may be utilized instead. Furthermore, this type of mold, particularly if the slurry is preheated and contains the carbon dioxide-consuming alkali, allows the heat to be applied directly over a large area of the slurry, permitting an extremely fast set.

After having set in molds, the blocks or slabs

which are formed are self-supporting before they are dry and while containing substantially the same amount of moisture as in the slurry before it has set. The blocks or slabs formed in other commercial processes where pressure molding is necessary are not self-supporting, and consequently have to be supported in frames after they are removed from the molds, so that they will not break during handling prior to drying thereof.

Upon removal of the slabs or blocks from the molds after setting thereof, they are next dried in the usual manner heretofore employed for drying the mechanically molded product. Such drying is accomplished, usually, in conventional drying ovens at a temperature ranging from one hundred fifty-five degrees Fahrenheit (155° F.) to three hundred ninety-five degrees Fahrenheit (395° F.), to remove all uncombined or free water not existing as water of crystallization. Depending on the temperature and the draft, it will take from twenty-four to seventy-two (24 to 72) hours for the drying. The drying, if desired, may be air drying, but oven drying is preferred because it is faster. Should the material tend to stick to the molds upon removal therefrom, the molds may be first greased with any suitable substance, such as petroleum grease.

Even though there is substantially no shrinkage of the material in the molds, it may be desirable to mill or trim the surfaces of the dried product so as to provide an attractive product not marred with surface imperfections. This is particularly true with respect to the type of molds, such as an open pan, wherein a relatively large surface area of the slurry is uncovered or exposed, as the exposed area tends to leave a surface which is not smooth. Not over ten percent. (10%) of the product need be removed by such milling when molds which expose a relatively large area of the slurry are employed, whereas with products produced by other methods wherein molding under pressure is required, the amount of product removed by milling runs from thirty percent. (30%) to forty percent. (40%). The milled-off material is not entirely waste material because it may be used for making magnesia insulating cement. However, it has less value as a cement, and therefore results in an economic loss. Hence, because of the lesser amount of material which need be trimmed from the block or slab of our invention when molds which expose a relatively large area of the slurry are employed, a further economy results. Because the product of our invention sets in a quiescent state substantially without shrinkage, the molds may be made of special shapes so as to form correspondingly shaped insulating fittings.

Standard commercial products of magnesium carbonate insulating blocks produced by former pressure molding methods contain about eighty-five percent (85%) by weight of basic magnesium carbonate as a bonding agent and about fifteen percent. (15%) by weight of asbestos fiber to reinforce the product. Under present standards, such blocks weigh from sixteen to eighteen pounds (16 to 18 lbs.) per cubic foot; the specific gravity, therefore, ranging from twenty-five one-hundredths (.25) to twenty-eight one-hundredths (.28). By adjustment of the water content of the slurry prior to casting it into the mold, the similar product of our invention containing the same percentages of basic magnesium carbonate and asbestos fiber can be made to weigh as low as nine pounds (9 lbs.) per cubic foot, and will average from ten to twelve pounds (10 to 12 lbs.) per cubic foot; the specific gravity, therefore, ranging from fourteen one-hundredths (.14) to nineteen one-hundredths (.19). The product of our invention will, thus, average from thirty-five percent. (35%) to forty-five percent. (45%) lighter than the corresponding product produced by former methods; and even though lighter, it is much stronger. This comparison between eighty-five percent. (85%) magnesium carbonate blocks of our invention and those heretofore produced holds true for any given specification of materials and percentages of magnesium carbonate in the respective blocks. Because of the lightness of the product of our invention, considerable saving in freight charges obtains. Also, due to the low density of our product, it has a lower heat conductivity coefficient than that of products produced by former methods. The heat conductivity coefficient of the product of our invention weighing about ten to twelve pounds (10 to 12 lbs.) per cubic foot will run about twenty percent. (20%) to thirty percent. (30%) lower than the product produced by former methods and weighing about sixteen to eighteen pounds (16 to 18 lbs.) per cubic foot.

Although the product of our invention is lighter, it is much stronger than heretofore produced products. Weight for weight, it is fifty percent (50%) to one hundred percent. (100%) stronger; while a block of our invention, for example an eighty-five percent (85%) magnesium carbonate block weighing eleven pounds (11 lbs.) per cubic foot, will be as strong or even stronger than the corresponding block produced by former methods and averaging sixteen to eighteen pounds (16 to 18 lbs.) per cubic foot.

As was previously related, where dolomitic material is the source of raw material, the calcium carbonate may be left in the slurry containing the self-setting magnesium carbonate crystals, subsequently treated by our preferred method to effect setting thereof, and still produce a satisfactory light-weight block adapted for heat insulating purposes. In this connection, the dolomitic product resulting from the method of our invention and containing the same percentage of asbestos fiber as occurs in the standard commercial magnesium heat-insulating blocks produced by former pressure molding methods, and in which calcium carbonate is not eliminated, can be made to weigh as low as twelve to sixteen pounds (12 to 16 lbs.) per cubic foot (the specific gravity, hence, ranging from about one hundred ninety-two one-thousandths (.192) to two hundred fifty-six one-thousandths (.256)). In addition to lightness the dolomitic product possesses greater strength and has higher insulating efficiency than the product produced by other commercial methods involving pressure molding, even though, in such other methods, the calcium compounds are eliminated from the source of dolomitic material. For example, a block formed by the method of our invention, weighing about fourteen pounds (14 lbs.) per cubic foot, is stronger than a sixteen pound (16 lb.) per cubic foot block produced by other commercial methods involving mechanical pressure and in which calcium carbonate is eliminated from the dolomitic material. Yet such block resulting from our method will have about twenty-five percent. (25%) greater insulating efficiency.

The product of our invention because of its light weight, is highly porous, i. e., cellular in structure, which is one of the factors enabling it to have a high heat insulating efficiency. Fur-

thermore, although the product is shaped, it is not stony or rock-like in character as are artificial stones or natural rocks, but is chalk-like in character. In other words, compared to an artificial stone or natural rock, it is relatively soft or crushable; the material being readily rubbed off from the surface thereof. However, insofar as magnesia insulation is concerned, the final dried product of our invention is relatively hard and firm or rigid, with sufficient strength and cohesive bonding power to provide a modulus of rupture (flexure strength) enabling such product to be entirely self-supporting in slabs as thin as one (1) inch and as long as three (3) feet. Such strength is necessary for allowing the material to be handled and applied. Not only is the final dried product self-supporting but, as previously explained, the set product prior to drying is also *self-supporting*.

The results of our invention are obtainable, irrespective of whether or not the composition to be set consists essentially of the self-setting, normal hydrated magnesium carbonate crystals alone or of such magnesium carbonate crystals intermixed with other materials. Therefore, in the appended claims, the expression "magnesium carbonate composition" includes compositions, such as the dolomitic composition described, which contain materials in addition to magnesium carbonate.

We claim:

1. In the method of producing a self-set magnesium carbonate composition from a slurry containing normal magnesium carbonate crystals having self-setting properties independent of application of pressure, said composition being capable of use as a heat insulating material, the step of enhancing setting of such slurry by adding *an alkali thereto to consume carbon dioxide* which is evolved during the setting.

2. In the method of producing a self-set magnesium carbonate composition from a slurry containing normal magnesium carbonate crystals having self-setting properties independent of application of pressure, said composition being capable of use as a heat insulating material, the step of enhancing setting of such slurry by adding magnesium oxide thereto to consume carbon dioxide which is evolved during the setting.

3. In the method of producing a self-set magnesium carbonate composition from a slurry containing precipitated normal magnesium carbonate crystals having self-setting properties independent of application of pressure, said composition being capable of use as a heat insulating material, the step of incorporating borax in such slurry.

4. In the method of producing a self-set magnesium carbonate composition from a slurry containing precipitated normal magnesium carbonate crystals having self-setting properties independent of application of pressure, said composition being capable of use as a heat insulating material, the step of incorporating an alkali metal hydroxide in such slurry.

5. A molded light weight cellular chalk-like but substantially rigid and self-supporting basic magnesium carbonate composition capable of use as a heat insulating material and self-set substantially without shrinkage independent of application of pressure from normal magnesium carbonate crystals having self-setting properties, said composition being strengthened by the product resulting from the addition thereto of a carbon dioxide-consuming alkali.

6. A molded light weight cellular chalk-like but substantially rigid and self-supporting basic magnesium carbonate composition capable of use as a heat insulating material and self-set substantially without shrinkage independent of application of pressure from normal magnesium carbonate crystals having self-setting properties, said composition being strengthened by the product resulting from the addition thereto of the magnesium oxide.

7. A molded light weight cellular chalk-like but substantially rigid and self-supporting basic magnesium carbonate composition capable of use as a heat insulating material and self-set substantially without shrinkage independent of application of pressure from normal magnesium carbonate crystals having self-setting properties, said composition being strengthened by the product resulting from the addition thereto of borax.

8. A molded light weight cellular chalk-like but substantially rigid and self-supporting basic magnesium carbonate composition capable of use as a heat insulating material and self-set substantially without shrinkage independent of application of pressure from normal magnesium carbonate crystals having self-setting properties, said composition being strengthened by the product resulting from the addition thereto of an alkali metal hydroxide.

9. A magnesium carbonate composition capable for the preparation of heat insulating material and having self-setting properties independent of application of pressure comprising a self-settable slurry containing needle-like crystals of normal magnesium carbonate having self-setting properties, said slurry also having sufficient alkali added thereto to neutralize any magnesium bicarbonate which may occur therein and consume carbon dioxide which is evolved during setting of the slurry.

10. The method of producing a self-set magnesium carbonate composition which comprises forming in a reaction vehicle a precipitate of normal magnesium carbonate in the form of needle-like crystals having self-setting properties, without allowing setting of such precipitate in the reaction vehicle removing from the reaction vehicle a slurry containing such precipitate, incorporating a carbon dioxide-consuming alkali in said precipitate to allow the subsequent setting thereof to be expedited, effecting the setting by applying heat to the slurry, and drying the resultant product.

11. The method of producing a self-set molded magnesium carbonate composition which comprises forming in a reaction vehicle a precipitate of normal magnesium carbonate in the form of needle-like crystals having self-setting properties, without allowing setting of such precipitate in the reaction vehicle removing from the reaction vehicle a slurry containing such precipitate, incorporating a carbon dioxide-consuming alkali to allow the subsequent setting to be expedited, either before or after the incorporation of said carbon dioxide-consuming alkali preheating said slurry to cooperate in expediting the setting, casting the preheated slurry into a form adapted to shape said composition, effecting the setting by applying heat to the slurry in the form, and drying the resultant product.

12. In the method of setting a magnesium carbonate composition by application of heat to a slurry containing normal magnesium carbonate in the form of needle-like crystals having self-setting properties; the step of expediting the set-

ting by preheating the slurry prior to effecting setting thereof.

13. In the method of producing a self-set molded magnesium carbonate composition by application of heat to a slurry in a form adapted to shape the composition and which contains normal magnesium carbonate in the form of needle-like crystals having self-setting properties; the steps of expediting the setting by preheating the slurry prior to casting it into said form, and either before or after such preheating incorporating a carbon dioxide-consuming alkali.

14. A basic magnesium carbonate composition self-set independent of application of pressure by conversion from normal magnesium carbonate crystals having self-setting properties, said composition being strengthened by the product resulting from the addition thereto of a carbon dioxide-consuming alkali.

19. A molded light weight cellular chalk-like but substantially rigid and self-supporting basic magnesium carbonate heat insulating composition reenforced by asbestos fiber, self-set independent of application of pressure without shrinkage by conversion from normal magnesium carbonate crystals having self-setting properties; said composition being characterized by the absence of fissures resulting from the incorporation therein of a carbon dioxide-consuming alkali.

16. The method of producing a self-set basic magnesium carbonate composition capable of use as a heat insulating material which comprises forming in an aqueous reaction vehicle a precipitate of normal magnesium carbonate in the form of needle-like crystals having self-setting properties, without allowing setting of such precipitate in the reaction vehicle removing from the reaction vehicle a slurry containing such precipitate, adding sufficient alkali to neutralize any magnesium bicarbonate which may occur and to consume carbon dioxide which is evolved during the setting, either before or after the addition of said alkali preheating the slurry to cooperate in expediting the setting, casting the preheated slurry into a form adapted to shape said composition, effecting the setting by applying heat to the slurry in the form while simultaneously precluding evaporation of substantial amounts of moisture from the setting slurry to minimize shrinkage during the setting, and drying the resultant product.

SAMUEL A. ABRAHAMS.
RUBIN LEWON.

CERTIFICATE OF CORRECTION.

Patent No. 2,209,754. July 30, 1940.

SAMUEL A. ABRAHAMS, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 10, for "2112,698" read --212,698--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 17th day of September, A. D. 1940.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.

Patented Jan. 11, 1944 2,339,041

UNITED STATES PATENT OFFICE

2,339,041

SELF-SET MAGNESIUM CARBONATE COMPOSITION AND METHOD FOR PREPARING THE SAME

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No Drawing. Application January 21, 1941, Serial No. 375,163

3 Claims. (Cl. 106—286)

Our invention relates to magnesium carbonate compositions, and more particularly to an improved method for enhancing the setting properties of magnesium carbonate prepared to possess self-setting properties and to an improved final product.

As is disclosed in our assignee's United States Patents Nos. 2,209,752, 2,209,753, and 2,209,754, all dated July 30, 1940 a self-setting magnesium carbonate composition adapted for use as a sound or heat insulating material may be prepared from various sources of materials; such as by reaction in an aqueous vehicle of a magnesium compound, such as sea water bittern, with a carbonate salt such as sodium carbonate; by decomposition of an aqueous solution of magnesium bicarbonate; and by passing with carbon dioxide-containing gas an aqueous vehicle containing a suspension of magnesium hydroxide. In the case where dolomitic material is used as the source of raw material, as is disclosed in Patent No. 2,209,754, the inherent lightness of the final product resulting from the self-setting properties thereof, enables the slurry containing both the calcium carbonate which is insoluble and the self-setting magnesium carbonate crystals to be set as such.

Such self-setting magnesium carbonate exists in the form of very fine, small crystals, and is a normal hydrated magnesium carbonate, believed to be the tri-hydrate. As is pointed out in the patents referred to, it is desirable to obtain relatively small crystals because small crystals have been found to provide greater strength in the final product than that obtainable by larger crystals; and to enhance the formation of relatively fine, small crystals, care must be taken to maintain proper temperature conditions because if the temperature of the reaction vehicle should be too high, the relatively fine, small crystals would be either totally or partially destroyed, resulting in loss or impairment of their self-setting properties. Also, excessive agitation is desirable during formation of the crystals, as it has been found that excessive agitation promotes the formation of the desirable smaller crystals.

The chemistry of magnesium carbonate is quite peculiar inasmuch as it is capable of undergoing many transformations during preparation thereof. Therefore, to obtain the desired relatively fine, small self-settable magnesium carbonate crystals, great care must be observed in the preparation thereof, which is sometimes burdensome in commercial manufacture of such crystals. This is especially so with respect to the preparation of such crystals by decomposition of an aqueous solution of magnesium bicarbonate in the manner disclosed in our assignee's Patent No. 2,209,752. Our invention has as its objects, among others, the provision of a method for promoting with minimum care the formation of the desired relatively small, fine magnesium carbonate crystals, particularly with respect to the decomposition method of Patent No. 2,209,752, and the provision of an improved final product resulting from such method. Other objects of our invention will become apparent from a perusal of the following description thereof.

We have found that uniform formation of the desired relatively fine, self-settable normal magnesium carbonate crystals may be obtained with minimum care by causing precipitation of such crystals in the aqueous reaction vehicle in the presence of any suitable colloidal dispersion of any suitable bentonite clay. The bentonite may be added to the aqueous reaction vehicle either before formation of the self-settable crystalline magnesium carbonate precipitate or just after formation of such precipitate commences, but it is more desirable to add the bentonite prior to the formation of such crystals in order to insure that the major part of such crystalline precipitate occurs in the presence of bentonite so that the bentonite may be readily effective. Except for the addition of the bentonite, the procedures for obtaining such self-settable crystals are the same as those described in the previously mentioned patents, wherein precipitation of such crystals is effected under excessive or vigorous agitation, and the temperature is maintained below the point at which the self-setting properties of such crystals would be destroyed or impaired. With respect to the decomposition method of Patent No. 2,209,752 in which the employment of bentonite is particularly applicable, it is desirable to maintain the temperature close to the highest temperature which may be safely employed without impairing the self-setting properties of the crystals. However, such temperature should not be much over one hundred twenty degrees Fahrenheit (120° F.); although if care is taken, a temperature as high as one hundred forty degrees Fahrenheit (140° F.) may be employed in such decomposition method.

The bentonite insures or promotes formation of the desired relatively fine, small crystals by inhibiting the growth thereof, and causes such crystals to be more uniform in size. Hence, such bentonite materially improves the final product by providing increased strength resulting from the fact that the crystals will all be of the de-

sired relatively fine and small substantially uniform size. This insures against formation of alternate hard and soft spots in the final set product, which might otherwise obtain should the crystals not be all of substantially the same relatively small size when the slurry containing them is subjected to setting conditions.

The character of the colloidal suspension or dispersion of the bentonite is not critical, as any of the well-known colloidal dispersions thereof may be employed, but it is preferred to utilize an aqueous dispersion because of the aqueous character of the reaction vehicles. A suitable well-known dispersion which we have found extremely satisfactory is formed by treating about one (1) part by weight of bentonite with about seventeen (17) parts by weight of hot water at a temperature of about one hundred twenty-five degrees Fahrenheit (125° F.) to two hundred twelve degrees Fahrenheit (212° F.), and thoroughly dispersing the bentonite in the water to form a colloidal suspension. Agitation may be employed to disperse the bentonite but we preferably subject the suspension to a colloidal mill so as to obtain more uniform dispersion. In this connection, it is preferred to treat the aqueous bentonite suspension with any suitable peptizing agent to facilitate the dispersion. Alkalies are generally most frequently employed commercially as peptizing agents for the bentonite. Any suitable alkali will do, but we prefer to utilize sodium carbonate as the peptizing agent, in an amount about one-tenth per cent (0.1%) by weight of the amount of bentonite in the suspension.

The minimum amount of bentonite to be added to the reaction vehicle is not particularly critical but should be sufficient to promote with ease the formation of the desired uniform relatively small, fine magnesium carbonate self-settable crystals. Usually about one half per cent (½%) to about two and one-half per cent (2½%) by weight of bentonite with reference to the calculated amount of normal magnesium carbonate tri-hydrate precipitable in the reaction vehicle, will suffice; and enough of the aqueous bentonite dispersion should be employed to provide the desired amount of bentonite. The maximum amount of bentonite is governed solely by practical considerations, as excessive quantities of bentonite have no adverse effect on the self-setting properties of the magnesium carbonate crystals. We have employed with satisfactory results, as much as five per cent (5%) by weight of bentonite with reference to the calculated amount of magnesium carbonate tri-hydrate precipitable in the reaction vehicle.

However, if quantities of bentonite amounting to more than five per cent (5%) by weight of the calculated amount of magnesium carbonate tri-hydrate are employed, it usually becomes very difficult to filter the resultant slurry because of the colloidal nature thereof imparted to it by the bentonite suspension. Also, the addition of larger quantities of bentonite may be undesirable because of too great an adulteration of the final product. Hence, the upper limit of the amount of bentonite suspension that may be added is determined by these practical factors.

The usual types of reenforcing materials, such as asbestos or other suitable reenforcing fiber, in an amount sufficient to provide a final product which contains from ten per cent (10%) to fifteen per cent (15%) by weight of the fiber may be intermixed with the slurry to be set; such product being generally that employed commercially for heat insulating purposes. Other chemically inactive solid bodies such as vermiculite or diatomaceous earth, may be also mixed in the slurry. Such inert filler or reenforcing fiber may be mixed directly in the slurry after it is formed, or if desired, they may be incorporated in the reaction vehicle in which the self-setting magnesium carbonate crystals are formed.

After the self-settable magnesium carbonate slurry containing the fine crystal promoting bentonite is formed in the reaction vehicle, the procedure for setting the product is preferably that outlined in Patent No. 2,209,754, starting at line 65, column 2, page 2 of the specification thereof, which brings out the steps of preferably preheating the slurry to shorten the time of setting; preferably adding a carbon dioxide-consuming alkali to the slurry to consume carbon dioxide as conversion from the normal to the basic carbonate occurs during the setting and thereby increases the strength of the final product; casting the slurry into a form or mold adapted to shape the composition; effecting the setting independent of application of pressure by applying heat to the slurry in the form while maintaining it in a quiescent state, and simultaneously precluding evaporation of substantial amounts of moisture from the setting slurry to minimize shrinkage; and drying the resultant product. Except for the increased strength which bentonite imparts to the final product, the bentonite will have no adverse effect on the various steps employed for setting the product.

The resultant set basic magnesium carbonate product, even though containing bentonite, possesses all the characteristics outlined in the specification of Patent No. 2,209,754, starting at line 75, column 2, of page 4, namely it is relatively light weight, rigid, and self-supporting. Internally, it is cellular in structure; and it has a chalk-like appearance. When the preferred quantity of bentonite previously outlined is employed and the set, final dried insulating product is made to contain about fifteen per cent (15%) by weight of asbestos fiber, the percentage of bentonite therein is about six-tenths of one per cent (0.6%) to about three per cent (3%) by weight of the final product. Such small quantity will not materially affect the specific gravity values of the products noted in Patent No. 2,209,754.

Employment of the bentonite to produce the results of our invention may be either in a reaction vehicle in which the self-setting precipitate consists essentially of normal hydrated magnesium carbonate crystals alone, or of such crystals intermixed with other materials, such as calcium carbonate which may remain when dolomitic material is employed as the source of raw material. Therefore, in the appended claims, the expression "magnesium carbonate composition" includes compositions, such as the dolomitic composition referred to, which contain materials in addition to magnesium carbonate.

We claim:

1. In the method of producing a self-set magnesium carbonate composition capable of use as a heat insulating material wherein a precipitate of self-settable normal magnesium carbonate crystals is formed in an aqueous reaction vehicle; the step of causing formation of such precipitate in the presence of a colloidal bentonite dispersion to promote relatively small and fine crystals for increasing the strength of the final product.

2. The method of producing a set magnesium

carbonate composition which comprises forming in an aqueous reaction vehicle a precipitate of normal magnesium carbonate in the form of crystals having self-setting properties, causing formation of such precipitate in the presence of a colloidal bentonite dispersion to promote relatively small and fine crystals, casting a slurry containing such precipitate and bentonite into a form adapted to provide the shape of the final product, and applying heat to the slurry in the form to enhance setting of such slurry to a firm cake.

3. The method of producing a set magnesium carbonate composition which comprises decomposing magnesium bicarbonate in solution by application of heat and agitation of the solution to provide a precipitate of normal magnesium carbonate in the form of crystals having self-setting properties, causing formation of such precipitate in the presence of a colloidal bentonite dispersion to promote relatively small and fine crystals, casting a slurry containing such precipitate and bentonite into a form adapted to provide the shape of the final product, and applying heat to the slurry in the form to enhance setting of such slurry to a firm cake.

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