Office de la Propriété Intellectuelle du Canada
Un organisme d'Industrie Canada

Canadian Intellectual Property Office
An agency of Industry Canada

CA 2208150 C 2004/03/23

(11)(21) 2 208 150

(12) BREVET CANADIEN
CANADIAN PATENT

(13) C

(22) Date de dépôt/Filing Date: 1997/06/18

(41) Mise à la disp. pub./Open to Public Insp.: 1998/12/18

(45) Date de délivrance/Issue Date: 2004/03/23

(51) Cl.Int.^{6}/Int.Cl.^{6} C01F 11/18

(72) Inventeurs/Inventors:
PORTER, ALVIN LEE, CA;
WILSON, WILLIAM JOSEPH, CA

(73) Propriétaire/Owner:
GRAYMONT (NB) INC., CA

(74) Agent: SIM & MCBURNEY

(54) Titre : PRODUCTION DE CARBONATE DE CALCIUM PRECIPITE A COULEUR AMELIOREE
(54) Title: MANUFACTURE OF PRECIPITATED CALCIUM CARBONATE OF IMPROVED COLOUR

(57) Abrégé/Abstract:
A method for the manufacture of precipitated calcium carbonate from impure calcium oxide of improved colour is disclosed. The method comprises admixing impure calcium oxide with an aqueous solution consisting essentially of a salt of at least one compound selected from the group consisting of organic amines of the formula RNH_2 and alkanolamines of the formula $NH_2(R^1OH)$, where R and R^1 are alkyl groups of 1-4 carbon atoms, and hydrochloric or nitric acid. The solution obtained is treated with a reducing agent e.g. sodium hydrosulphite, separated from insoluble matter and then treated with carbon dioxide or the carbonate of the amine or alkanolamine. Preferably, the amine of the salt and of the carbonate are the same, and the salt is used in at least the stoichiometric amount to dissolve the lime.

ABSTRACT OF THE DISCLOSURE

A method for the manufacture of precipitated calcium carbonate from impure calcium oxide of improved colour is disclosed. The method comprises admixing impure calcium oxide with an aqueous solution consisting essentially of a salt of at least one compound selected from the group consisting of organic amines of the formula RNH_2 and alkanolamines of the formula $NH_2(R^1OH)$, where R and R^1 are alkyl groups of 1-4 carbon atoms, and hydrochloric or nitric acid. The solution obtained is treated with a reducing agent e.g. sodium hydrosulphite, separated from insoluble matter and then treated with carbon dioxide or the carbonate of the amine or alkanolamine. Preferably, the amine of the salt and of the carbonate are the same, and the salt is used in at least the stoichiometric amount to dissolve the lime.

MANUFACTURE OF PRECIPITATED CALCIUM CARBONATE OF IMPROVED COLOUR

The present invention relates to a method for the manufacture of precipitated calcium carbonate (PCC) from lime using ethanolamine or an organic amine. In particular, the method provides a precipitated calcium carbonate with a high brightness.

Precipitated calcium carbonate is used in a wide variety of end uses. In some end uses, the brightness of the precipitated calcium carbonate is of minor importance. However, in a number of end uses e.g. use of precipitated calcium carbonate as a filler, as a coating agent or as a pigment, it is important or critical that the precipitated calcium carbonate have a high degree of brightness. As used herein, brightness of calcium carbonate is measured by the method of TAPPI T646 om-94. Use of precipitated calcium carbonate as a filler, coating agent or pigment frequently requires that the brightness be not less than 95%.

A number of techniques may be used to obtain precipitated calcium carbonate. A typical method involves forming a suspension of lime in water, converting the lime into calcium hydroxide, and treating the resultant suspension of calcium hydroxide with carbon dioxide so as to form calcium carbonate. Such treatment leaves grit, colored material and other insoluble matter in the suspension, which contaminates the resulting PCC that is formed. Thus, in order to obtain PCC with acceptable properties, the lime used in the process must be of a high purity.

Canadian application No. 2 203 210 of W.J. Wilson and A.L. Porter, filed April 21, 1997, discloses admixing impure calcium oxide with an aqueous solution of a salt of an organic amine or alkanolamine with hydrochloric or nitric acid, and separating the resultant solution and recovering PCC. Such a method overcomes problems associated with dissolution of lime with ammonium nitrate or ammonium chloride in that, if carbon dioxide and air

is used to precipitate the calcium carbonate, then a significant part of the cost of the process is the capital and operating cost of the scrubbing of ammonia from the exit gas, which is a mixture of ammonia, carbon dioxide and air.

U.S. Patent 4 900 533 of P.J. Malden discloses slaking calcium oxide in water, cooling the suspension to 45°C or lower, and then carbonating the suspension in water with carbon dioxide in the presence of a dithionite bleaching agent.

A method for the manufacture of precipitated calcium carbonate using an organic amine or alkanolamine of improved brightness has now been found.

Accordingly, an aspect of the present invention provides for a method for the manufacture of precipitated calcium carbonate with a high brightness from impure calcium oxide, comprising:

(a) admixing said impure calcium oxide with an aqueous solution consisting essentially of a salt of at least one compound selected from the group consisting of organic amines of the formula RNH_2 and alkanolamines of the formula $NH_2(R^1OH)$, where R and R^1 are alkyl groups of 1-4 carbon atoms, and hydrochloric or nitric acid;

(b) adding a solution of a reducing agent to the solution of (a);

(c) separating the solution so obtained from insoluble matter therein; and

(d) treating the solution with (i) carbon dioxide or (ii) the carbonate of said amine or alkanolamine of step (a).

In a preferred embodiment of the method of the present invention, the salt is added in step (i) in at least the stoichiometric amount to dissolve the lime.

In another embodiment, the reducing agent is added in an amount effective to reduce the colour of the solution of (a).

In a further embodiment, the reducing agent is sodium hydrosulphite, which is added in an amount to _____

effect a reduction in colour of the solution subjected to separation in step (c) and an improvement in the brightness of the PCC obtained in step (d). In embodiments, the sodium hydrosulphite is added to the aqueous solution in step (a) prior to admixing of the impure calcium oxide.

In a still further embodiment, the ratio of the salt of organic amine or alkanolamine to water, on a weight basis, is in the range of 1:1 to 1:3.

In yet another embodiment, the temperature of the solutions is at least 70°C and especially at least 75°C.

In another embodiment, the solution of (a) is additionally treated for separation of insoluble matter therein prior to step (b).

In yet another embodiment, the method of the present invention provides precipitated calcium carbonate having a brightness of at least 95%, and especially at least 97%.

The method of the present invention relates to the manufacture of precipitated calcium carbonate from impure lime. Sources of impure lime are known and may be obtained from the calcination of limestone in an industrial kiln. Sources of limestone suitable for a calcination process are known to persons skilled in the art. It is understood that the limestone would be contaminated with magnesium carbonate and that other materials may also be present, some of which might be colored. Examples of the latter could include iron oxide, manganese oxide, iron carbonate, manganese carbonate, sand and other silicates. Calcination of the limestone may be carried out at temperatures in the range of from about 950°C to about 1100°C, especially in the range of from about 950°C to about 1050°C. Magnesium is not solubilized in the process of the present invention if the temperature of calcination is above 900°C. Nonetheless, it is understood that any suitable source of lime may be used for the process.

The lime is slaked by admixing with a reagent solution in an aqueous solution in which the calcium will dissolve. The reagent solution is an aqueous solution of a salt of at least one compound selected from the group consisting of organic amines of the formula RNH_2 and alkanolamines of the formula $NH_2(R^1OH)$, where R and R^1 are alkyl groups of 1-4 carbon atoms. Such amines are primary amines and the alkanolamines only have one -OH moiety. The preferred alkyl groups are methyl and ethyl. The organic amine is in the form of a salt with hydrochloric acid or nitric acid.

In order to increase the concentration of PCC ultimately obtained in the method, and thereby reduce the amount of aqueous solution that must be handled during operation of the method, it is preferred to increase the concentration of the salt of the organic amine or alkanolamine in the solution used to treat the lime i.e. in step (a) of the method described above. However, it is found, as least in some embodiments of lime that may be used in the process, that there is a tendency for the formation of colour in the solution of step (a). The formation of such colour is detrimental to the brightness of the PCC that is ultimately obtained. As an example, if ethanolamine hydrochloride is used as the amine, then with some sources of lime, colour may be formed as the concentration of ethanolamine hydrochloride is increased above 1 part ethanolamine hydrochloride to 3 parts of water. The colour of the solution obtained is typically brown in nature.

In the method of the present invention, the solution of (a) is treated with a reducing agent. In particular, the solution is treated with a reducing agent that does not result in precipitation of a calcium compound in any significant amount. The amount of reducing agent may be varied, and is used in an amount effective to reduce the colour of the solution of (a). In a preferred embodiment, the reducing agent is present in the aqueous solution of

(a) prior to addition of the impure calcium oxide, which tends to prevent formation of colour, especially brown colour.

Examples of the reducing agent include sodium hydrosulphite, also known as sodium dithionite ($Na_2S_2O_4$), and sodium sulphite. Sodium hydrosulphite is preferred.

The resultant solution is filtered so as to remove impurities such as grit and other contaminants that have not dissolved in the solution. While the solution is filtered after the addition of reducing agent, the solution may additionally be filtered prior to addition of the reducing agent.

The filtered solution is then reacted in one of two ways viz a) with carbon dioxide or b) with an amine carbonate. In preferred embodiments, the amine of the amine carbonate is the same as the amine in the aqueous solution used to solubilize the lime. This results in precipitation of calcium carbonate which, after filtration, leaves a mother liquor that is suitable for reuse. Use of carbon dioxide gas is also a preferred method of effecting precipitation of calcium carbonate, because a consequence of the use of organic amine or alkanolamine in step (a) is the option to recover excess carbon dioxide in step (d), which may readily be accomplished. The precipitated calcium carbonate that is filtered from the solution is washed, to purify the calcium carbonate and wash off amine for recycling to the process. In preferred embodiments of the method, the calcium carbonate that is obtained is in the range of 97+% purity.

The ratio of the salt of organic amine or alkanolamine, especially ethanolamine hydrochloride, to water, on a weight basis may be at least 1:1, especially in the range 1:1 to 1:3, although ratios with higher amounts of water may be used. Use of ratios in the range of 1:1 to 1:3 results in a significant decrease in the volume of the solution obtained on precipitation of the

PCC, which must be processed for recovery of PCC. Ratios of 1:1 or close to that ratio are preferred.

Heating of the solution containing PCC in the form of a suspension prior to recovery of the PCC may be used to effect a change in the crystal form of the PCC. For instance, heating of the solution to 80°C tends to effect a change of the crystals to, or facilitate formation of, scalenohedral crystals. Heating to 100°C results in aragonite crystals. In addition to the effects on the type of crystal obtained, heating of the solution results in a decrease in solution viscosity. The heated solution is more readily filtered.

Passing of carbon dioxide into the solution obtained with a 1:1 mixture tends to result in formation of a gel of PCC, which may be converted to a crystalline form. During such conversion, the particle size of the crystals may be controlled e.g. particle sizes in the range of 0.5 to 1 micron may be obtained.

The product obtained has a high brightness, as measured by the method of TAPPI T646 om-94. In preferred embodiments, the PCC has a brightness of at least 97%. In addition, the PCC obtained from the process is essentially free of grit and insolubles, in contrast to the conventional method of preparing PCC, and is therefore believed to be a PCC of high quality. The absence of grit means that the product can be used without being abrasive to calendering rolls in paper making processes.

It has also been found that under the conditions of preparation, only traces of magnesium carbonate are found in the resulting product, primarily because the magnesium tends not to dissolve in the slaking process and therefore is filtered out prior to carbonation.

The PCC obtained by the process of the present invention may be prepared in a variety of crystalline forms, depending on the temperature of crystallization, as is well known in the art. For example, at 10 to 15°C,

the product is obtained as rhombohedral crystals, while at 35 to 40°C vaterite crystals are obtained. This metastable form of calcium carbonate may be converted to aragonite crystals, which are obtained in the form of needles, by heating to about 95°C.

While processing with CO_2 in general tends to give coarse crystals, i.e. greater than 1 micron in size, mixing of solutions of ethanolamine carbonate with the reaction mixture can give gelatinous products which with stirring causes crystals to grow. After a period of time, which in embodiments and depending on the particular solution might be about 30 minutes, the crystals grow to an appropriate size, e.g. in the range of where the majority of the crystals are less than 1 micron.

Thus by varying the reaction conditions, temperatures and concentrations, it is possible to obtain PCC products in a wide range of particle sizes. This provides versatility to the process and extends the potential application of the invention.

The present invention is illustrated by the following examples.

EXAMPLE I

In a comparative experiment, 100 grams of a sample of lime were slaked in 1000 ml of water, and the resultant suspension was passed through a 325 mesh screen to remove solid matter. The temperature of the resultant solution was raised to 40°C, and then carbon dioxide gas was passed through the solution.

The precipitated calcium carbonate that was obtained was examined by electron microscopy, and found to be scalenohedral crystals with a size of about 1 micron. The brightness was measured, using an elrepho brightness meter according to the method of TAPPI T646 om-94, and found to be 82.2.

The procedure was repeated, with sodium

hydrosulphite added to the solution at 40°C prior to passing carbon dioxide through the solution. The brightness of the resultant precipitated calcium carbonate was found to be 91.4.

EXAMPLE II

Ethanolamine chloride was prepared by mixing 2207 grams of ethanolamine with 3819 grams of concentrated hydrochloric acid, to give a 1:2 solution of ethanolamine hydrochloride in water. 1125 grams of the lime of Example I were added to the solution, which was then stirred for a period of one hour. The solution was brown in colour.

500 ml of the solution that was obtained were heated to 80°C, following which 2 gm of sodium hydrosulphite were added. The solution was stirred for five minutes, and filtered to remove residue. The resultant solution was very slightly yellow in colour.

200 ml of the solution obtained was maintained at 80°C, and carbon dioxide was passed through, with continuous stirring, until a pH of 6.35 was reached. The solution was then filtered, and the filtrate was washed with water containing carbon dioxide, at a temperature of 80°C.

The crystals of the calcium carbonate obtained were rhombohedral, and had a brightness of 97.8.

This example shows that the method of the present invention provides PCC with substantially improved brightness.

EXAMPLE III

In separate experiments, the above procedure was repeated with and without the addition of sodium hydrosulphite. It was found that when the sodium hydrosulphite was added, the PCC obtained had a brightness of 97.6. In contrast, when the sodium hydrosulphite was omitted, the PCC obtained had a

brightness of only 91.1.

This example illustrates the substantial improvement in brightness of the PCC obtained at high concentrations of ethanolamine hydrochloride, when sodium hydrosulphite is added at high temperatures (80°C) to the brown solution of the slurry of lime, and filtered.

CLAIMS

1. A method for the manufacture of precipitated calcium carbonate with a high brightness from impure calcium oxide, comprising:

(a) admixing said impure calcium oxide with an aqueous solution consisting essentially of a salt of at least one compound selected from the group consisting of organic amines of the formula RNH_2 and alkanolamines of the formula $NH_2(R^1OH)$, where R and R^1 are alkyl groups of 1-4 carbon atoms, and hydrochloric or nitric acid;

(b) adding a solution of a reducing agent to the solution of (a);

(c) separating the solution so obtained from insoluble matter therein; and

(d) treating the solution with (i) carbon dioxide or (ii) the carbonate of said amine or alkanolamine of step (a).

2. The method of Claim 1 in which the salt is added in step (i) in at least the stoichiometric amount to dissolve the lime.

3. The method of Claim 1 or Claim 2 in which the reducing agent is added in an amount effective to reduce the colour of the solution of (a).

4. The method of Claim 3 in which the reducing agent is sodium hydrosulphite, which is added in an amount to effect a reduction in colour of the solution subjected to separation in step (c) and an improvement in the brightness of the PCC obtained in step (d).

5. The method of any one of Claims 1-4 in which the sodium hydrosulphite is added to the aqueous solution in step (a) prior to admixing of the impure calcium oxide.

6. The method of any one of Claims 1-5 in which the ratio of the salt of organic amine or alkanolamine to water, on a weight basis, is in the range of 1:1 to 1:3.

7. The method of any one of Claims 1-6 in which the solution of (a) is additionally treated for separation of insoluble matter therein prior to step (b).

8. The method of any one of Claims 1-7 in which the temperature of the solutions is at least 70°C.

9. The method of Claim 8 in which the precipitated calcium carbonate has a brightness of at least 95%.

10. The method of Claim 9 in which the brightness is at least 97%.

11. The method of any one of Claims 1-10 in which the solution is treated, in step (d), with an alkanolamine carbonate.

12. The method of any one of Claims 1-10 in which the solution is treated, in step (d), with an amine carbonate.

13. The method of any one of Claims 1-10 in which the solution is treated, in step (d), with carbon dioxide.

14. The method of any one of Claims 1-13 in which the organic amine is ethanolamine.