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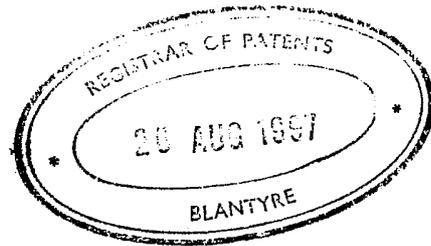
(51) **International Patent Classification (Int.Cl.7):** C01F 11/18

(54) **Title:** Production Of Precipitated Calcium Carbonate

(57) **Abstract:** A process for producing precipitated calcium carbonate in a pipe reactor having a series of inlet points and an outlet point, includes the steps of introducing carbon dioxide gas at a pressure of from 1 bar into the pipe reactor at an inlet point A; and introducing ammonia gas at a pressure of from 1 bar into the pipe reactor at an inlet point B upstream or preferably downstream of the inlet point A to contact the carbon dioxide gas with the ammonia in the pipe reactor in the presence of water. Thereafter, for a batch process, to produce fine particles, there is introduced into the pipe reactor a solution of calcium nitrate at an inlet point C upstream of the inlet point A and the inlet point B, while controlling the temperature in the reactor to below 58°C and the pH in the pipe reactor in the range of from 6,5 to 9,0 to produce a product containing calcium carbonate in particulate form at the outlet point; recycling the product from the outlet point to the inlet point C; and repeating these steps until the calcium carbonate particles reach the desired particle size. Alternatively, for a continuous process which produces coarser particles, there is introduced into the pipe reactor a solution of calcium nitrate at an inlet point D between the inlet point A and the inlet point B or downstream of the inlet point A and the inlet point B, while controlling the temperature in the pipe reactor to below 58°C and the pH in the pipe reactor in the range of from 6,5 to 9,0, to produce a product containing calcium carbonate in particulate form at the outlet point.

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BACKGROUND OF THE INVENTION

This invention relates to a process for the production of precipitated calcium carbonate.

Precipitated calcium carbonate is used in many industrial processes as a filler or pigment. The main industries which use precipitated calcium carbonate are the paper, PVC and coatings industries. For this purpose the precipitated calcium carbonate needs to have a fine particle size and in some cases a specific shape.

Many processes are known for the production of precipitated calcium

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carbonate. One known process involves reacting brown lime (Ca(OH)_2) and ammonium nitrate (NH_4NO_3) to give calcium nitrate ($\text{Ca(NO}_3)_2$) and ammonium hydroxide (NH_4OH). After filtration of the inert substances, the resultant solution is carbonated with carbon dioxide gas to form precipitated calcium carbonate and to reform the ammonium nitrate. While this process gives a pure product, the product is coarse.

Precipitated calcium carbonate is also used in the production of a high purity lime product. For this purpose, the precipitated calcium carbonate must have a coarse particle size.

There is a need for a new process for the production of precipitated calcium carbonate, which process can produce either fine particles or coarse particles as desired.

SUMMARY OF THE INVENTION

According to the invention there is provided a process for producing precipitated calcium carbonate (CaCO_3) in a pipe reactor having a series of inlet points and an outlet point, which includes the steps of:

- (1) introducing carbon dioxide gas at a pressure of from 1 bar into the pipe reactor at an inlet point A;
- (2) introducing ammonia gas at a pressure of from 1 bar into the pipe reactor at an inlet point B upstream or preferably downstream of the inlet point A to contact the carbon dioxide gas with the ammonia gas in the pipe reactor in the presence of water;

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and either

- (3)(i) introducing a solution of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) into the pipe reactor at an inlet point C upstream of the inlet point A and the inlet point B, while controlling the temperature in the pipe reactor to below 58°C and the pH in the pipe reactor in the range of from 6,5 to 9,0, to produce a product containing calcium carbonate in particulate form at the outlet point;
- (ii) recycling the product of step (3)(i) from the outlet point to the inlet point C; and
- (iii) repeating steps (3)(i) and (3)(ii) until the calcium carbonate particles reach the desired particle size;

or

- (4) introducing a solution of calcium nitrate into the pipe reactor at an inlet point D between the inlet point A and the inlet point B or downstream of the inlet point A and the inlet point B, while controlling the temperature in the pipe reactor to below 58°C and the pH in the pipe reactor in the range of from 6,5 to 9,0, to produce a product containing calcium carbonate in particulate form at the outlet point.

The process of steps (1), (2) and (3) is a batch process, which produces fine particles of precipitated calcium carbonate preferably having a particle size D_{50} of less than 2 microns, while the process of steps (1), (2) and (4) is a continuous process which produces coarse particles of precipitated calcium carbonate having a particle size D_{50} of greater than 5 microns.

The carbon dioxide is preferably introduced into the pipe reactor at a pressure of about 7 bar.

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The ammonia gas is preferably introduced into the pipe reactor at a pressure of about 7 bar.

The pH in the pipe reactor is preferably from 6,5 to 8,5 inclusive, more preferably about 7,2.

The temperature in the pipe reactor is preferably from 20°C to 40°C inclusive.

The calcium nitrate solution may be produced by reacting calcium hydroxide with ammonium nitrate to give the calcium nitrate solution and ammonium hydroxide. The ammonium hydroxide so produced may be recycled. Further, the ammonium nitrate used may be recycled.

Alternatively, the calcium nitrate solution may be produced by reacting calcium carbonate with nitric acid to produce the solution of calcium nitrate, carbon dioxide and water.

The calcium carbonate may be used in the form of dolomite comprising calcium carbonate and magnesium carbonate. When the dolomite is treated with nitric acid, there is produced calcium nitrate and magnesium nitrate. The magnesium may be precipitated as magnesium hydroxide, giving a solution of calcium nitrate for use in the process.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a flow diagram of a plant for use in a batch process for producing precipitated calcium carbonate according to the

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invention;

Figure 2 is a flow diagram of a plant for use in a continuous process for producing precipitated calcium carbonate according to the invention;

Figure 3 is a graph of particle diameter distribution from a batch process for producing precipitated calcium carbonate according to the invention; and

Figure 4 is a graph of particle diameter distribution for a continuous process for producing precipitated calcium carbonate according to the invention.

DESCRIPTION OF EMBODIMENTS

As stated above, the process of the invention may either be a batch process or a continuous process. Both processes must be carried out in a pipe reactor having a series of inlets and an outlet.

In the batch process, illustrated in Figure 1, carbon dioxide gas, at a pressure of from 1 bar, preferably at about 7 bar, is introduced into the pipe reactor 10 at an inlet point A. Thereafter, ammonia gas at a pressure of from 1 bar, preferably about 7 bar, is introduced into the pipe reactor 10 at an inlet point B downstream of the inlet point A. The carbon dioxide gas and the ammonia gas react in the presence of water in the pipe reactor 10 to produce ammonium carbonate $((\text{NH}_4)_2\text{CO}_3)$.

The reaction is carried out at a suitable temperature below 58°C , which is the dissociation temperature of ammonium carbonate, preferably at a temperature of from 20°C to 40°C inclusive. The pH in the pipe reactor

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10 must be from 6,5 to 9,0 inclusive, preferably from 6,5 to 8,5 inclusive, more preferably about 7,2.

While both the carbon dioxide gas and the ammonia gas are introduced into the pipe reactor 10 at a pressure preferably of about 7 bar, the pressure drops within the pipe reactor 10 so that the pressure at the outlet 12 from the pipe reactor 10 will be less than 7 bar.

Thereafter, a solution of calcium nitrate is introduced into the pipe reactor 10 at an inlet point C upstream of the inlet point A to produce a product containing calcium carbonate in particulate form at the outlet point 12. The product from the outlet point 12 is recycled to the inlet point C and this is repeated until the calcium carbonate particles reach the desired particle size.

Generally, the pipe reactor will be connected to a holding tank 14 filled with calcium nitrate solution. The calcium nitrate solution is transported from the holding tank 14 via a pump 16 to the inlet point C where it is introduced into the pipe reactor 10. The product produced at the outlet 12 of the pipe reactor 10 is then recycled back to the holding tank 14 and the process is continued until the desired particle size is reached.

Generally, the calcium nitrate solution from the holding tank 14 is introduced into the pipe reactor 10 at the inlet point C at a pressure of from 14 bar. As mentioned above, the pressure drops in the pipe reactor 10 so that the pressure at the outlet 12 of the pipe reactor 10 is generally about 3 bar.

When the desired particle size is reached, the product may be passed from

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the holding tank 14 to a pressure filter 18, from which exits the final product.

This batch process gives fine particles of precipitated calcium carbonate, generally having a particle size D_{50} of less than 2 microns.

In the continuous process, illustrated in Figure 2, carbon dioxide gas, at a pressure of from 1 bar, preferably at about 7 bar, is introduced into the pipe reactor 10 at an inlet point A. Thereafter ammonia gas at a pressure of from 1 bar, preferably at about 7 bar, is introduced into the pipe reactor 10 at an inlet point B downstream of the inlet point A. A solution of calcium nitrate is introduced into the pipe reactor 10 at an inlet point D downstream of the inlet point A and between the inlet points A and B, i.e. between the point of introduction of the carbon dioxide gas and the ammonia gas. As a result, there is no formation of ammonium carbonate which is then reacted with the calcium nitrate, but rather a reaction whereby the calcium carbonate is produced directly from the three reactants.

Again, this process is carried out at a suitable temperature below 58°C, preferably at a temperature of from 20° to 40°C inclusive, and at a pH of from 6,5 to 9,0 inclusive, preferably from 6,5 to 8,5 inclusive, more preferably about 7,2.

As this is a continuous process, generally the reactants pass only once through the pipe reactor 10. However, if desired, a portion of the material produced at the outlet 12 of the pipe reactor 10 may be recycled to the inlet D of the pipe reactor, to increase the particle size.

The product from the outlet 12 may be passed to a pressure filter 18, from

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which exits the final product.

The continuous process gives particles of precipitated calcium carbonate with a particle size D_{50} of greater than 5 microns. This particle size may be increased with recycling as described above.

This coarse material is of particular use in the making of a high purity lime product.

The solution of calcium nitrate may have any desired concentration. Suitable concentration for the calcium nitrate solution is 10 to 50% inclusive by mass.

Obviously, the relative quantities of the calcium nitrate solution, ammonia gas and carbon dioxide used are dependent on the stoichiometry of the reaction. It is useful to carbonate at a slight excess of ammonium carbonate to obtain a high degree of purity. After completion, any excess carbonate in the liquor may be destroyed by the addition of nitric acid to a pH of about 7 before the liquor is further used.

The calcium nitrate may be prepared in any suitable manner. Three examples are set out below.

- 1 Brown lime is treated with ammonium nitrate to give calcium nitrate and ammonium hydroxide.



The ammonium hydroxide is flashed off by agitation and heat (95-100°C) and may be used to contact the carbon dioxide gas.

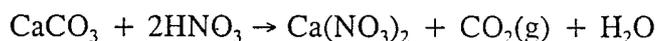
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The ammonium nitrate used may be recycled from the end of the process.

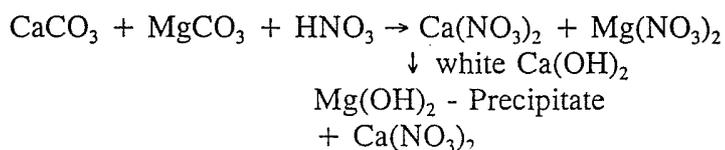
- 2 Impure calcium carbonate is treated with nitric acid to give calcium nitrate, carbon dioxide and water.



The pH of the calcium nitrate solution is raised whereby the transition metal oxides precipitate. After filtration there is left a relatively pure calcium nitrate solution.

The ammonium nitrate formed using this calcium nitrate may be used in other products such as fertilizer and explosives. This particular process is thus a once through process without recycling of the ammonium nitrate.

- 3 Dolomite (comprising calcium carbonate and magnesium carbonate) is treated with nitric acid to give calcium nitrate and magnesium nitrate. This is then treated with white calcium hydroxide to precipitate the pure magnesium hydroxide.



The calcium nitrate may then be used in the process.

Alternatively $\text{NH}_3(\text{g})$ may be used to precipitate $\text{Mg}(\text{OH})_2$, with the formation of NH_4NO_3 which may be recycled.

The $\text{Ca}(\text{NO}_3)_2$ and $\text{Mg}(\text{NO}_3)_2$ can also be reacted with $\text{NH}_3(\text{g})$ under a pressure of greater than 7 bar to give $\text{Mg}(\text{OH})_2$ and a higher concentration

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of NH_4NO_3 , which thus requires less evaporation.

The magnesium hydroxide may be calcined to pure MgO .

An example of a pilot plant run of the process of the invention will now be given.

A feed pump was started to circulate the calcium nitrate solution. A sample of the solution was also taken to measure the concentration accurately.

Approximately 235 litres of solution were then transferred to a pipe reactor by controlling the flow rate through a rotameter constantly for 20 minutes. The feed pump was left running to keep an even concentration of calcium nitrate throughout the run. Water was injected through a nipple and water line for a short while to ensure suction for the pump. The pump was then started to circulate the calcium nitrate solution. Ammonia and carbon dioxide gases were then sparged in the pipe reactor. Ammonia was sparged in at 8 bar and a rotameter reading of 25%. Carbon dioxide was sparged in at 8 bar and a rotameter reading of 14%. Both gases were allowed to flow into the pipe reactor for 45 minutes.

To run the process continuously calcium nitrate was fed in at 33% rotameter reading and the gases were left to flow continuously. This was allowed to go on until the slurry or holding tank was full. A large recycle was allowed during the continuous process and only a small stream was drawn off via the hose pipe that transfers to the slurry holding tank.

Whilst running the reaction continuously four full filter holding tanks of

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slurry were filtered. This was because a counter-current cake washing simulation was done. Basically the next slurry filtration was done first with water, and then with the last half of the previous filtrate. Eighty litres were used to filter each slurry. Samples of the slurry were taken. Every ten litres of filtrate was also sampled to measure ammonium nitrate content. Records of flow rate of filtrate, volume, time and pressure were also taken to enable scale up. Samples of the filter cake were also taken to measure particle size and moisture content.

Figure 3 is a graph of particle diameter distribution for a batch process of the invention, and Figure 4 is a graph of particle diameter distribution for a continuous process of the invention, as described above.

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CLAIMS

1 A process for producing precipitated calcium carbonate in a pipe reactor having a series of inlet points and an outlet point includes the steps of:

- (1) introducing carbon dioxide gas at a pressure of from 1 bar into the pipe reactor at an inlet point A;
- (2) introducing ammonia gas at a pressure of from 1 bar into the pipe reactor at an inlet point B upstream or downstream of the inlet point A to contact the carbon dioxide gas with the ammonia gas in the pipe reactor in the presence of water;

and either

- (3)(i) introducing a solution of calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) into the pipe reactor at an inlet point C upstream of the inlet point A and the inlet point B, while controlling the temperature in the pipe reactor to below 58°C and the pH in the pipe reactor in the range of from 6,5 to 9,0 inclusive, to produce a product containing calcium carbonate in particulate form at the outlet point;
- (ii) recycling the product of step (3)(i) from the outlet point to the inlet point C; and
- (iii) repeating steps (3)(i) and (3)(ii) until the calcium carbonate particles reach the desired particle size;

or

- (4) introducing a solution of calcium nitrate into the

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pipe reactor at an inlet point D between the inlet point A and the inlet point B or downstream of the inlet point A and the inlet point B, while controlling the temperature in the pipe reactor to below 58°C and the pH in the pipe reactor in the range of from 6,5 to 9,0 inclusive, to produce a product containing calcium carbonate in particulate form at the outlet point.

- 2 A process according to claim 1 which includes steps (1), (2) and (3) and which is a batch process.
- 3 A process according to claim 1 which includes steps (1), (2) and (4) and which is continuous process.
- 4 A process according to any one of claims 1 to 3 wherein in step (2) the ammonia gas is introduced into the pipe reactor at an inlet point B downstream of the inlet point A.
- 5 A process according to any one of claims 1 to 4 wherein in step (1) the carbon dioxide is introduced into the pipe reactor at a pressure of about 7 bar.
- 6 A process according to any one of claims 1 to 5 wherein in step (2) the ammonia gas is introduced into the pipe reactor at a pressure of about 7 bar.
- 7 A process according to any one of claims 1 to 6 wherein the pH in the pipe reactor is from 6,5 to 8,5 inclusive.

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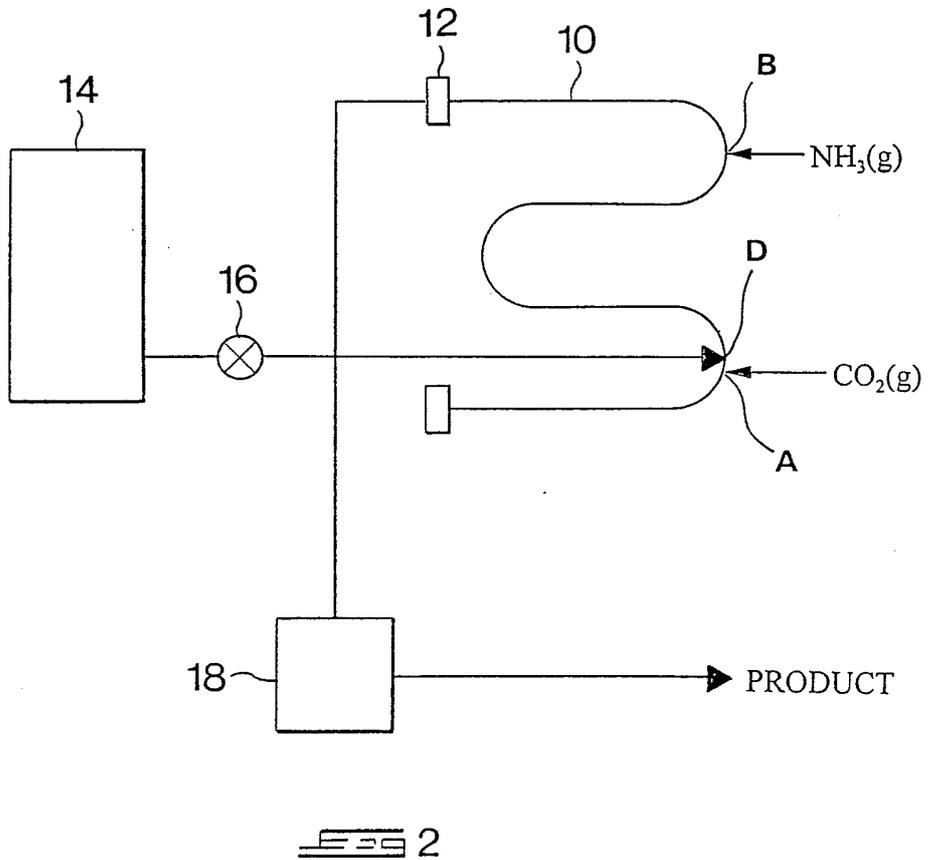
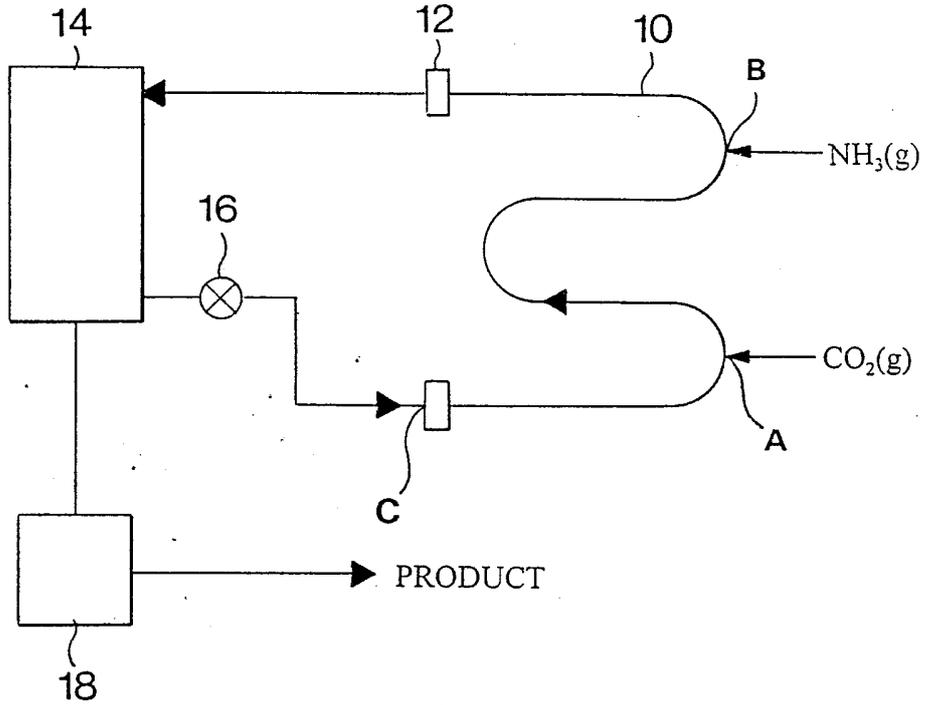
- 8 A process according to claim 7 wherein the pH in the pipe reactor is about 7.2.
- 9 A process according to any one of claims 1 to 8 wherein the temperature in the pipe reactor is from 20°C to 40°C inclusive.

FISHER, CORMACK & BOTHA
Patent Agents for the Applicant
Dated this 14 day of August 1997

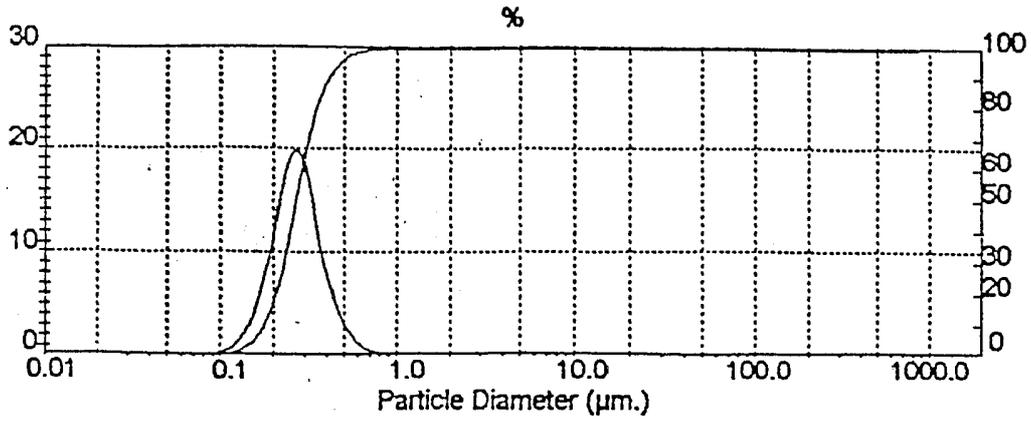


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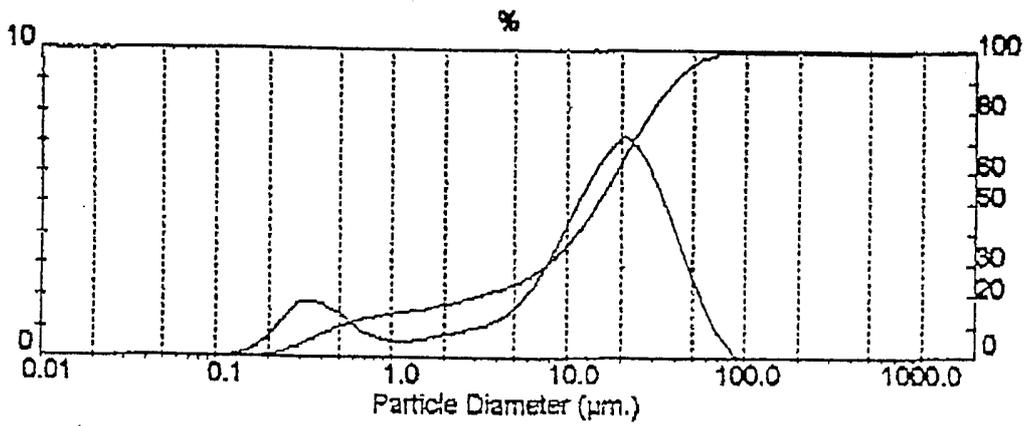
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