### INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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**Title:** PROCESS FOR THE PREPARATION OF INORGANIC FOAMING AGENT MASTERBATCH

**Abstract**

An inorganic foaming agent is economically and readily produced in the form of a masterbatch by melt-extruding one of the major components of the inorganic foaming agent with a carrier resin to prepare an intermediate masterbatch and blending the intermediate masterbatch with a composition containing the remaining component(s) or all of the components constituting the inorganic foaming agent.
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PROCESS FOR THE PREPARATION OF INORGANIC FOAMING AGENT MASTERBATCH

Field of the Invention

The present invention relates to a novel process for preparing an inorganic foaming agent in the form of a masterbatch, by using an intermediate masterbatch.

Background of the Invention

Foaming agents are widely used in such conventional processes as extrusion, calendering, injection molding, coating, expansion casting and rotation molding of plastics. Hitherto, organic foaming agents such as azodicarbonamides have been mainly used due to the large amounts of gas generated and the low cost thereof. However, the organic foaming agent has the critical deficiency of entailing harmful materials, which can cause an environmental problem, such as harmful materials during the production process of an organic foaming agent and ammonia gas during the foaming process thereof.

Generally, inorganic foaming agents known in the prior art contain polycarboxylic acids and inorganic carbonates. However, the use of the acid/carbonate blowing agent may cause a premature reaction by acid/base reaction or with water and the premature reaction is accelerated by the presence of water. Accordingly, most of commercially available inorganic foaming agents have been marketed with each of their components coated with a coating agent, e.g., stearic acid, monoglyceride, silane coupling agent and the like.

Various coating methods and materials for each component of the inorganic foaming agent are disclosed, for example, in U.S. Patent Nos. 5,009,809; 5,009,810;
5,037,580; 5,045,570; 5,106,534 and 5,137,655. However, such coating methods generally suffer from a high processing cost due to the requirements of using the additional coating procedure and expensive coating agent.

Summary of the Invention

It is, therefore, a primary object of the invention to provide a process for the production of an inorganic foaming agent in the form of a masterbatch at a low cost.

In accordance with one aspect of the present invention, there is provided a process for economical production of an inorganic foaming agent masterbatch, which comprises melt-extruding one of the major components of the inorganic foaming agent with a carrier resin to prepare an intermediate masterbatch; and then blending the intermediate masterbatch with a composition containing the remaining component(s) or all of the components constituting the inorganic foaming agent.

Detailed Description of the Invention

The inorganic foaming agent generally contains a polycarboxylic acid or a salt thereof and an inorganic carbonate as major constituents thereof. The polycarboxylic acid may be generally represented by the formula HOOC-R-COOH wherein R is a C_{1-25} alkylene group which may contain one or more hydroxy substituents and, optionally, unsaturated group(s).

Representative of the polycarboxylic acid and salts thereof which may be employed include citric acid, fumaric acid, tartaric acid, sodium hydrogen citrate, monosodium citrate and mixtures thereof, which may be employed alone or in combination. Further, the inorganic carbonate may be preferably a carbonate containing an alkali or alkaline
earth metal such as Ca, K, Mg, Na and the like; and
exemplary compounds thereof include sodium bicarbonate,
potassium bicarbonate and mixtures thereof, which may be
employed alone or in combination.

Any thermoplastic resin may be employed as a carrier
resin for the inorganic foaming agent masterbatch of the
present invention.

The term "masterbatch", as used herein, represents an
encapsulated ingredient concentrate with a carrier resin.
Such masterbatch is typically prepared by melt-extruding the
ingredients thereof with the carrier resin. However, in the
case of an inorganic foaming agent, such conventional
masterbatch preparation method cannot be employed due to the
premature reaction by acid/base reaction or premature
reaction with water.

In accordance with the inventive process, therefore, in
order to prevent such premature reaction of the major
components of the inorganic foaming agent, first, one of the
components is encapsulated with a carrier resin at a
temperature ranging from 40 to 235°C using a conventional
extruder, e.g., a single or twin screw extruder having one
or two inlets, to prepare an intermediate masterbatch in the
form of a pellet. The component constituting the
intermediate masterbatch may be preferably employed in an
amount of 5 to 60 parts by weight per 100 parts by weight of
the carrier resin.

Subsequently, the intermediate masterbatch is blended
with a composition containing the remaining component(s)
constituting the inorganic foaming agent to produce an
inorganic foaming agent masterbatch as a final product. The
composition containing the remaining component(s) may be in
the form of a coated powder, an uncoated raw powder or a
melt-extruded intermediate masterbatch separately prepared
by the inventive process.

Alternatively, the intermediate masterbatch may be
blended with a composition containing all of the components constituting the inorganic foaming agent. The composition is preferably prepared in such a form that the components cannot be reacted with each other, e.g., a mixture of a coated powder of each component, or a mixture of melt-extruded intermediate masterbatches of respective components separately prepared.

The inorganic foaming agent masterbatch of the present invention may optionally comprise wax, slip agent, lubricant and the like in an effective amount.

The inventive process has a number of advantages: expensive coating materials and procedures may be avoided; the step of preparing an inorganic foaming agent and the step of preparing a masterbatch are integrated into one step to shorten the preparation process; the inorganic foaming agent masterbatch thus obtained still has a good foamability comparable to a masterbatch of a conventional inorganic foaming agent produced by the prior art; and cell size and the amount of gas generated from the foaming agent can be easily controlled by adjusting the mix ratio of the constituents of the inorganic foaming agent.

The following Examples are given for the purpose of illustration only and are not intended to limit the scope of the invention.

In the Examples, as a carrier resin, a polyethylene is the one having a melt index of 45 g/10min as measured in accordance with ASTM D-1238 and a density of 0.915 g/cm³ as measured in accordance with ASTM D-1505; an ethylene vinyl acetate copolymer is the one having a melt index of 45 g/10min as measured in accordance with ASTM D-1238; a polystyrene is the one having a melt index of 16 g/10min as measured in accordance with ASTM D-1238 and a density of 1.05 g/cm³ as measured in accordance with ASTM D-1505; a styrene-butadiene copolymer is the one having a butadiene monomer content of 25% and a melt index of 8 g/10min.
Further, wax used in the Examples is the one having a softening point of 109°C and a number average molecular weight of 3,000, which is prepared by thermally decomposing of a polyethylene resin.

Example 1

In a Henschel mixer (a dry mixer), 94.5 parts by weight of polyethylene as a carrier resin, 5 parts by weight of wax and 0.5 part by weight of calcium stearate were blended for 5 minutes, and the blend was introduced into an inlet of a twin screw extruder and melt-extruded at a temperature ranging from 40 to 235°C and a speed ranging from 50 to 200 rpm. During the melt-extrusion of the blend, 45 parts by weight of sodium bicarbonate was introduced into another inlet of the extruder to formulate and extrude it with the blend. The extruder was designed to be temperature-controlled at nine portions. The extrudate was cooled in a water bath at room temperature and then cut to obtain a sodium bicarbonate masterbatch in the form of a pellet.

Separately, in accordance with the procedure as above, 66 parts by weight of polyethylene, 31 parts by weight of anhydrous citric acid and 3 parts by weight of wax were employed to obtain a citric acid masterbatch.

Finally, the respective masterbatches prepared above were blended at a weight ratio of 50:50 in a tumbler mixer to obtain a desired inorganic foaming agent masterbatch.

Example 2

97 parts by weight of the citric acid masterbatch prepared in Example 1, 2 parts by weight of sodium bicarbonate as a powder form and 1 part by weight of dioctyl phthalate, which was added to uniformly disperse the sodium bicarbonate powder into the citric acid masterbatch, were
blended for 5 minutes in a tumbler mixer to obtain a desired inorganic foaming agent masterbatch.

Example 3

100 parts by weight of polyethylene was introduced into an inlet of a twin screw extruder and melt-extruded at a temperature ranging from 40 to 235° C and a speed ranging from 50 to 200 rpm. During the melt-extrusion, 12 parts by weight of sodium bicarbonate was introduced into another inlet of the extruder to formulate and extrude it with the polyethylene resin. The extruder was designed to be temperature-controlled at nine portions. The extrudate was cooled in a water bath at room temperature and then cut to obtain a sodium bicarbonate masterbatch in the form of a pellet.

Separately, in accordance with the procedure as above, 12 parts by weight of anhydrous citric acid was employed to obtain a citric acid masterbatch.

Finally, the sodium bicarbonate masterbatch and the citric acid masterbatch prepared above were blended at a weight ratio of 30:70 in a tumbler mixer to obtain a desired inorganic foaming agent masterbatch.

Example 4

The procedure described in Example 1 was repeated except that monosodium citrate was employed instead of anhydrous citric acid to obtain a desired inorganic foaming agent masterbatch.

Example 5

In a Henschel mixer, 30 parts by weight of polyethylene, 63 parts by weight of polystyrene, 5 parts by
weight of styrene-butadiene copolymer and 2 parts by weight of zinc stearate were blended for 5 minutes, and the blend was introduced into an inlet of a twin screw extruder and melt-extruded at a temperature ranging from 40 to 235°C and a speed ranging from 50 to 200 rpm. The extrudate was cooled in a water bath at room temperature and then cut to obtain a resin mixture in the form of a pellet. The resulting resin pellet was introduced into an inlet of a twin screw extruder and melt-extruded at a temperature ranging from 40 to 235°C and a speed ranging from 50 to 200 rpm, and during the melt-extrusion of the resin mixture pellet, 10 parts by weight of sodium bicarbonate was introduced into another inlet of the extruder to formulate and extrude it with the resin mixture pellet. The extruder was designed to be temperature-controlled at nine portions. The extrudate was cooled in a water bath at room temperature and then cut to obtain a sodium bicarbonate masterbatch in the form of a pellet.

Separately, 80 parts by weight of polystyrene and 20 parts by weight of anhydrous citric acid were blended for 5 minutes in a Henschel mixer and melt-extruded by using a twin screw extruder at a temperature ranging from 40 to 235°C and a speed ranging from 50 to 200 rpm. The extrudate was cooled in a water bath at room temperature and then cut to obtain a citric acid masterbatch in the form of a pellet.

Finally, the sodium bicarbonate masterbatch and the citric acid masterbatch prepared in the above were blended at a weight ratio of 70:30 in a tumbler mixer to obtain a desired inorganic foaming agent masterbatch.

Example 6

The procedure employed in Example 1 was repeated except that ethylene vinyl acetate copolymer was employed as a carrier resin, to obtain a desired inorganic foaming agent
masterbatch.

Example 7

In a Henschel mixer, 70 parts by weight of styrene-
butadiene copolymer and 30 parts by weight of polyethylene
were blended for 5 minutes, and the blend was introduced
into an inlet of a twin screw extruder and melt-extruded at
a temperature ranging from 40 to 235°C and a speed ranging
from 50 to 200 rpm. During the melt-extrusion of the blend,
10 parts by weight of sodium bicarbonate was introduced into
another inlet of the extruder to formulate and extrude it
with the blend. The extruder was designed to be
temperature-controlled at nine portions. The extrudate was
cooled in a water bath at room temperature and then cut to
obtain a sodium bicarbonate masterbatch in the form of a
pellet.

Separately, 80 parts by weight of styrene-butadiene
copolymer and 20 parts by weight of anhydrous citric acid
were employed to obtain a citric acid masterbatch.

Finally, the sodium bicarbonate masterbatch and the
citric acid masterbatch prepared in the above were blended
at a weight ratio of 70:30 in a tumbler mixer to obtain a
desired inorganic foaming agent masterbatch.

Comparative Example 1

In a Henschel mixer, 91.5 parts by weight of
polyethylene as a carrier resin, 7 parts by weight of wax,
0.5 part by weight of oleamide and 1 part by weight of
calcium stearate were blended for 5 minutes, and the blend
was introduced into an inlet of a twin screw extruder and
melt-extruded at a temperature ranging from 40 to 235°C and
a speed ranging from 50 to 200 rpm. During the melt-
extrusion of the blend, 45 parts by weight of inorganic
foaming agent C#850 (a product of Dongjin Whasung Co., Ltd.) was introduced into another inlet of the extruder to formulate and extrude it with the blend. The extrudate was cooled in a water bath at room temperature and then cut to obtain an inorganic foaming agent masterbatch in the form of a pellet.

Comparative Example 2

The procedure described in Comparative Example 1 was repeated except that ethylene vinyl acetate copolymer was employed as a carrier resin.

Example 8

20 parts by weight of the inorganic foaming agent masterbatch prepared in Comparative Example 1 and 80 parts by weight of the sodium bicarbonate masterbatch prepared in Example 1 were blended for 5 minutes in a tumbler mixer to obtain a desired inorganic foaming agent masterbatch.

Example 9

20 parts by weight of the inorganic foaming agent masterbatch prepared in Comparative Example 1 and 80 parts by weight of the inorganic foaming agent masterbatch finally prepared in Example 1 were blended for 5 minutes in a tumbler mixer to obtain a desired inorganic foaming agent masterbatch.

Example 10

The procedure described in Example 3 was repeated except that tartaric acid was employed instead of anhydrous citric acid to obtain a desired inorganic foaming agent
masterbatch.

Example 11

The procedure described in Example 3 was repeated except that fumaric acid was employed instead of anhydrous citric acid to obtain a desired inorganic foaming agent masterbatch.

Example 12

The procedure described in Example 3 was repeated except that potassium bicarbonate was employed instead of sodium bicarbonate to obtain a desired inorganic foaming agent masterbatch.

Foamability Test 1

The sodium bicarbonate masterbatch prepared in Example 1 was blended with the citric acid masterbatch prepared in Example 1 in a tumbler mixer for 5 minutes at a mixing ratio of 2:1, 1:1 or 1:2 to obtain a mixed inorganic foaming agent masterbatch. 2 parts by weight of the mixed masterbatch was blended with 98 parts by weight of polyethylene TR-144 (a product of Daelim Industry Co., Ltd.) having a density of 0.945 g/cm³ in a tumbler mixer for 5 minutes, and the blend was extruded by using a twin screw extruder at a temperature ranging from 180 to 220°C to obtain a foamed polyethylene product.

As a control, 2 parts by weight of the inorganic foaming agent masterbatch produced in Comparative Example 1 was also employed to obtain a foamed product.

The foamed products were evaluated by measuring their densities using an automatic density tester (a product of DOYOSEIKI, Japan) and the results are shown in Table 1.
Table 1

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<td>Density (g/cm³)</td>
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Foamability Test 2

3 parts by weight of the inorganic foaming agent masterbatch produced in Example 6 was blended with 97 parts by weight of ethylene vinylacetate copolymer having a density of 0.935 g/cm³ and a melt index of 3g/10min. in a tumbler mixer for 5 minutes, and the blend was extruded by using a single screw extruder at a temperature ranging from 180 to 220°C to obtain a foamed polyethylene product.

As a control, 3 parts by weight of the inorganic foaming agent masterbatch produced in Comparative Example 2 was also employed to obtain a foamed product.

The foamed products were evaluated by measuring their densities using an automatic density tester (a product of DOYOSEIKI, Japan) and the results are shown in Table 2.

Table 2

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<th>Masterbatch Employed</th>
<th>Example 6</th>
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<td>Density (g/cm³)</td>
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<td>0.78</td>
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As can be shown in Tables 1 and 2, the plastic product foamed by the inorganic foaming agent masterbatch produced in accordance with the inventive process has a lower density
(i.e., an excellent foamability) than those of the masterbatch produced by prior art methods.

While the invention has been described in connection with the above specific embodiments, it should be recognized that various modifications and changes may be made by those skilled in the art to the invention which also fall within the scope of the invention as defined by the appended claims.
What is claimed is:

1. A process for preparing an inorganic foaming agent having a number of components in the form of a masterbatch, which comprises melt-extruding one of the components with a carrier resin to prepare an intermediate masterbatch and further blending the intermediate masterbatch with a composition containing the remaining component(s).

2. The process of claim 1, wherein the composition is in the form of a coated powder, uncoated raw powder or melt-extruded masterbatch of the remaining component(s).

3. A process for preparing an inorganic foaming agent having a number of components in the form of a masterbatch, which comprises melt-extruding one of the components with a carrier resin to prepare an intermediate masterbatch and further blending the intermediate masterbatch with a composition containing all of the components constituting the inorganic foaming agent.

4. The process of claim 3, wherein the composition is in the form of a mixture of a coated powder of each of the components, or a mixture of melt-extruded masterbatches of the respective components.

5. The process of any one of claims 1 to 4, wherein the inorganic foaming agent contains a polycarboxylic acid having the formula of HOOC-R-COOH wherein R is a C₁₋₂₅ alkylene group including one or more hydroxy substituents and, optionally, an unsaturated group(s), or a salt thereof, and an inorganic carbonate as its components.

6. The process of claim 5, wherein the polycarboxylic acid or a salt thereof is selected from the group consisting
of citric acid, fumaric acid, tartaric acid, sodium hydrogen citrate, monosodium citrate and a mixture thereof; and the inorganic carbonate is selected from the group consisting of sodium bicarbonate, potassium bicarbonate and a mixture thereof.

7. An inorganic foaming agent produced in accordance with the process recited in any one of claims 1 to 6.

8. An intermediate masterbatch for producing an inorganic foaming agent having a number of components in the form of a masterbatch, prepared by melt-extruding one of the components with a carrier resin.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5: C 08 J 9/06, 9/08
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
IPC 5: C 08 J 9/06, 9/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPIL

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search
18 July 1994 (18.07.94)

Date of mailing of the international search report
22 August 1994 (22.08.94)

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