

AUSTRALIA
Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

We, BASF AKTIENGESELLSCHAFT being the person(s) identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

626433

[71] Applicant: BASF AKTIENGESELLSCHAFT
Address: D-6700 Ludwigshafen Germany

[70] Nominated Person: BASF AKTIENGESELLSCHAFT
Address: D-6700 Ludwigshafen Germany

[54] Invention Title: PREPARATION OF BEAD-FORM EXPANDABLE STYRENE POLYMERS

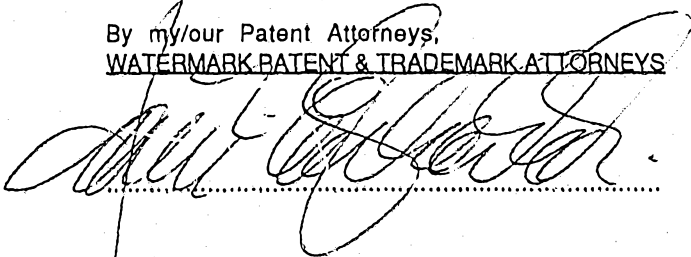
[72] Name(s) of actual inventor(s): HANS HINTZ, UWE GUHR, KLAUS HAHN, HANS GEORG KEPPLER

[74] Address for service in Australia: c/o WATERMARK PATENT & TRADEMARK ATTORNEYS, of
The Atrium, 290 Burwood Road, Hawthorn, Victoria 3122, Australia Attorney Code: WM

BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
P3921147.9	Germany	DE	28 June 1989 by BASF AKTIENGESELLSCHAFT

By my/our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS



Louis C. Gebhardt
Registered Patent Attorney

28/4/92
(Date)



AUSTRALIA

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NOTICE OF ENTITLEMENT
(To be filed before acceptance)

I/We, BASF AKTIENGESELLSCHAFT
of, D-6700 Ludwigshafen Germany

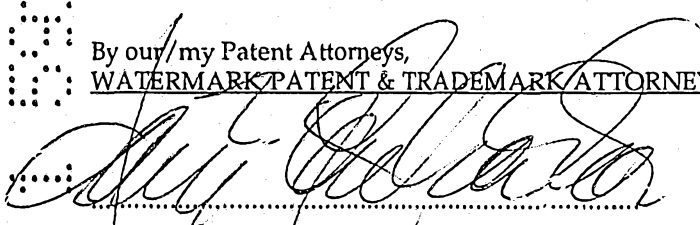
being the applicant in respect of Application No. 57848/90 state the following:-

The Person nominated for the grant of the patent:
has entitlement from the actual inventor: by assignment

The person nominated for the grant of the patent:
is the applicant of the basic application listed on the patent request form

The basic application listed on the request form:
is the first application made in a Convention country in respect of the invention

By our/my Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS


.....
Louis C. Gebhardt
Registered Patent Attorney

28/4/92
.....
(Date)

(12) PATENT ABRIDGMENT (11) Document No. AU-B-57848/90
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- (54) Title
PREPARATION OF BEAD FORM EXPANDABLE STYRENE POLYMERS
- International Patent Classification(s)
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- (21) Application No. : **57848/90** (22) Application Date : **27.06.90**
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3921147 28.06.89 DE FEDERAL REPUBLIC OF GERMANY
- (43) Publication Date : **03.01.91**
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- (71) Applicant(s)
BASF AKTIENGESELLSCHAFT
- (72) Inventor(s)
HANS HINTZ; UWE GUHR; KLAUS HAHN; HANS GEORG KEPPLER
- (74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122
- (56) Prior Art Documents
AU 620710 53908/90 C08J 9/20
AU 526349 57849/80 C08J 9/20
- (57) Claim

1. A process for the preparation of a bead-form expandable styrene polymer by polymerization of styrene, if desired with further comonomers, in aqueous suspension in the presence of customary suspension stabilizers and customary styrene-soluble polymerization catalysts and with addition of from 1 to 10% by weight of a C₃- to C₆- hydrocarbon as blowing agent and, if desired, customary additives in effective amounts, which comprises
- initiating the polymerization by rapidly heating the polymerizing batch to from 80 to 90°C within a maximum of 2 hours,
 - subsequently allowing the reaction temperature to increase to from 120°C to 130°C by from 8 to 17°C per hour, and wherein
 - the conversion is from 30 to 60% when 100°C is reached, and
 - the conversion is 80% or more when the maximum temperature is reached, and which comprises
 - subsequently keeping the batch at from 100 to 130°C until the residual monomer content in the polymer has dropped to less than 0.1%.
2. A process as claimed in claim 1, wherein the polymerization is carried out in the presence of a customary chain-transfer agent, in particular tert-dodecyl mercaptan, in an amount of from 0.0001 to 0.01% by weight, based on styrene.
3. Foam mouldings having a density of from 0.005 to 0.1g/cm³, characterised in that said foam mouldings are made of expandable styrene polymer produced in accordance with the process of claim 1 or claim 2.

COMMONWEALTH OF AUSTRALIA

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COMPLETE SPECIFICATION **626433**

(ORIGINAL)

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Complete Specification Lodged:
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Related Art :

Name of Applicant : BASF AKTIENGESELLSCHAFT

Address of Applicant : D-6700 Ludwigshafen, Federal Republic of Germany

Actual Inventor : HANS HINTZ, UWE GUHR, KLAUS HAHN, HANS GEORG KEPPLER

Address for Service : WATERMARK PATENT & TRADEMARK ATTORNEYS.
LOCKED BAG NO. 5, HAWTHORN, VICTORIA 3122, AUSTRALIA

* Complete Specification for the invention entitled:

PREPARATION OF BEAD-FORM EXPANDABLE STYRENE POLYMERS

The following statement is a full description of this invention, including the best method of performing it known to us

Preparation of bead-form expandable styrene polymers

5 The present invention relates to a process for
the preparation of bead-form expandable styrene polymers
having improved expandability. Foams based on styrene
polymers have achieved great industrial importance as
heat-insulating materials and packing materials. They are
produced on an industrial scale by first preparing
expandable styrene polymers by suspension polymerization
of styrene in the presence of a blowing agent, foaming
10 these styrene polymers by heating to form foam particles,
and subsequently welding the foam particles in molds to
form moldings.

15 The long reaction time in the suspension polymer-
ization and the unsatisfactory throughput during foaming
of the expandable styrene polymers to form foam beads
were regarded as disadvantageous.

20 It is an object of the present invention to
reduce the reaction time in the polymerization and
simultaneously to produce products which can be foamed at
high throughput without adversely affecting the
dimensional stability of the foam moldings produced
therefrom.

25 We have found, surprisingly, that these objects
are achieved by carrying out the reaction in a modified
manner.

30 The present invention relates to a process for
the preparation of bead-form expandable styrene polymers
by polymerization of styrene, if desired with further
comonomers, in aqueous suspension in the presence of
customary suspension stabilizers and customary styrene-
soluble polymerization catalysts and with addition of
from 1 to 10 percent by weight of a C₃- to C₆-hydrocarbon
as blowing agent and, if desired, customary additives in
effective amounts, which comprises

35 a) initiating the polymerization by rapidly heating the
polymerization batch to from 80 to 90°C within a
maximum of 2 hours,

- b) subsequently allowing the reaction temperature to increase up to from 120 to 130°C by from 8 to 17°C per hour, and wherein
- c) the conversion is from 30 to 60 % when 100°C is reached, and
- 5 d) the conversion is 80 % or more when the maximum temperature is reached, and which comprises
- e) subsequently keeping the batch at from 100 to 130°C until the residual monomer content of the polymer
- 10 has dropped to less than 0.1 %.

For the purposes of the invention, styrene polymers are polystyrene and copolymers of styrene with other α, β -olefinically unsaturated compounds containing 50 parts by weight of styrene or more in copolymerized form. Examples of suitable comonomers are α -methylstyrene, ring-halogenated styrenes, ring-alkylated styrenes, acrylonitrile, acrylates or methacrylates of alcohols having from 1 to 8 carbon atoms, N-vinyl compounds, such as vinyl carbazole, maleic anhydride or also small amounts of compounds containing two polymerizable double bonds, such as butadiene, divinylbenzene or butanediol diacrylate.

As blowing agents, the molding compositions contain from 1 to 10 % by weight, preferably from 2 to 8 % by weight, in particular from 3 to 7 % by weight, of a C₃- to C₆-hydrocarbon, such as propane, butane, isobutane, n-pentane, i-pentane, neopentane and/or hexane. A commercially available pentane mixture is preferably used.

The styrene polymers may also contain customary additives of other substances which impart certain properties to the expandable products. Examples which may be mentioned are flameproofing agents based on organic bromine or chlorine compounds, such as trisdibromopropyl phosphate, hexabromocyclododecane and chlorinated paraffin and synergists for flameproofing agents, such as dicumyl peroxide and highly unstable organic peroxides;

5 furthermore antistatic agents, stabilizers, dyes, lubricants, fillers and substances which have an anti-adhesive action during pre-foaming, such as zinc stearate, melamine-formaldehyde condensates or silica, and agents for shortening the demolding time during final foaming, for example glycerol esters or hydroxycarboxylates. Depending on the intended action, the additives may be homogeneously distributed in the particles or in the form of a surface coating.

10 The suspension polymerization of styrene is known per se. It is described in detail in Kunststoff-Handbuch, Volume V, Polystyrene, Carl Hanser-Verlag, pages 679 to 688. In this process, styrene, if appropriate together with the abovementioned comonomers is generally suspended in water, customary organic or inorganic suspension stabilizers being added, preferably in an amount of from 0.05 to 2 % by weight, based on the suspension.

15 The styrene polymers according to the invention are prepared by polymerization of styrene, if desired together with up to 50 % by weight of the abovementioned comonomers, in aqueous suspension, the above-described blowing agents and, if desired, customary additives in effective amounts being added before, during or after the polymerization.

20 It is also possible to carry out the polymerization in the presence of a customary chain-transfer agent which regulates the molecular weight. tert-Dodecyl mercaptan is preferably used. The regulator is generally used in an amount of from 0.0001 to 0.01 % by weight, based on styrene.

25 It is essential to the invention to initiate the polymerization by rapidly heating the polymerization batch to from 80 to 90°C. The batch is generally heated from room temperature up to from 80 to 90°C with stirring within 20 to 120 minutes, preferably 60 to 120 minutes.

30 It is furthermore essential to the invention that the reaction temperature is subsequently allowed to rise

to from 120 to 130°C by from 8 to 17°C per hour, preferably by from 9 to 15°C per hour. Since the reaction is exothermic, this rise in temperature is controlled by appropriate cooling.

5 It is moreover essential to the invention that the conversion is from 30 to 60 %, preferably from 30 to 55 %, in particular from 30 to 40 %, when 100°C is reached, i.e. 30 to 60 % of the conversion should take place during the increase in temperature to 100°C, which
10 can easily be monitored by appropriate sampling and analysis.

 It is also essential to the invention that the conversion is 80 % or more, preferably from 80 to 98 %, when the maximum temperature is reached (i.e. from 120 to
15 130°C), and that the batch is subsequently kept at from 100 to 130°C until the residual monomer content of the polymer has dropped to less than 0.1 %, preferably less than 0.09 %, in particular less than 0.08 %.

 The novel process makes it possible to shorten the reaction time by from 1 to 2 hours compared with the
20 conventional process.

 The temperature control according to the invention makes it possible to positively affect the molecular weight and the molecular weight distribution of the polymer and consequently the rheological properties which are
25 responsible for the expandability. The reduction in the melt extensibility which is thus achieved results in improved expandability. At the same melt extensibility, the reduction in the reversible elongation results in improved dimensional stability. Both properties can be
30 measured in accordance with the method in Prüfung hochpolymerer Werkstoffe, Carl Hanser Verlag, Vienna, 1977, page 422, as follows:

 The polymer particles are melted by heating to
35 155°C and degassed for 5 minutes to evaporate the blowing agent. A polymer strand having a length of 20 mm and a diameter of 5 mm is produced by extrusion. The sample is

clamped into a tension apparatus in hot silicone oil at 150°C. It is extended at a tensile stress of $2 \cdot 10^4$ Pa to a length of 300 mm. The melt extensibility μ is derived from a ratio of tensile force to a rate of elongation. After the tensile stress is released, the sample shrinks again. The reversible elongation E_r is the natural logarithm of the ratio of the initial length of the sample to the length of the sample after shrinkage.

The particulate, blowing agent-containing styrene polymers prepared according to the invention have a melt extensibility of less than $3.5 \cdot 10^6$ (Pas), preferably less than $3 \cdot 10^6$ (Pas), and a reversible elongation of less than 0.95, preferably less than 0.85, measured by the method described.

The blowing agent-containing styrene polymer particles prepared according to the invention generally have a diameter of from 0.2 to 4 mm. They can be pre-foamed by customary methods, for example using steam to give foam particles having a diameter of from 0.5 to 2 cm and a bulk density of from 0.005 to 0.1 g/cm³. It is apparent that the throughput is considerably increased here and that the bulk density is reduced under constant foam conditions.

The pre-foamed particles can then be subjected to final foaming by customary processes to give foam moldings having a density of from 0.005 to 0.1 g/cm³.

In the examples, parts and percentages are by weight.

The table shows the improved expandabilities according to the invention, as the throughput (kg/h) at comparable bulk densities, and the attendant melt extensibilities μ (Pas) and reversible elongations E_r , both reduced according to the invention.

EXAMPLE 1

1a Polymerization

A mixture of 150 parts of water, 0.1 part of sodium pyrophosphate, 100 parts of styrene, 0.15 part of

5 benzoyl peroxide and 0.25 part of t-butyl perbenzoate (as polymerization initiators) was heated to 85°C in the course of 2 hours with stirring in a pressure-tight stirred reactor made from stainless steel. The temperature was subsequently increased continuously to 120°C over the course of 3.5 hours. After 2 hours from 85°C, 2 parts of a 10 % strength aqueous solution of polyvinylpyrrolidone were added. After 3 hours from 85°C, 7 parts of pentane were metered into the stirred reactor. The mixture was then stirred at 120°C for a further 5 hours. The conversion was 50 % when 100°C had been reached and 98 % when the maximum temperature of 120°C had been reached. After 5 hours at 120°C, the polymer only had a styrene content of 0.09 %. The batch was subsequently cooled, and the polymer was separated off, washed and dried.

The granules obtained exhibited a mean particle diameter of 1.5 mm.

20 1b Coating
100 parts of the expandable polystyrene granules having a bead distribution of from 1.0 to 2.3 mm in diameter were pre-coated in a paddle mixer for 3 minutes with 0.4 part of glycerol monostearate.

25 1c Processing
The coated EPS beads were pre-foamed to a bulk density of 15 g/l ± 0.1 g/l in a continuous stirred foamer, Rauscher type, using flowing steam, and the throughput in kg/h was determined.

EXAMPLE 2

Polymerization

35 A mixture of 150 parts of water, 0.1 part of sodium pyrophosphate, 100 parts of styrene, 0.15 part of benzoyl peroxide and 0.25 part of t-butyl perbenzoate (as

polymerization initiators), 0.7 part of hexabromocyclodecane as flameproofing agent and 0.2 part of dicumyl peroxide as synergist was heated to 85°C over 100 minutes with stirring in a pressure-tight stirred reactor made from stainless steel. The temperature was subsequently increased continuously to 120°C over the course of 3 hours. After 1.5 hours from 85°C, 2 parts of a 10 % strength aqueous solution of polyvinylpyrrolidone were added. After 2.5 hours from 85°C, 7 parts of pentane were metered into the stirred reactor. The mixture was then stirred for a further 6 hours while the temperature was slowly reduced from 120 to 110°C. The conversion was 30 % when 100°C had been reached and 80 % when the maximum temperature of 120°C had been reached. After completion of the reaction, the polymer only had a styrene content of 0.09 %. The batch was subsequently cooled, and the polymer was separated off, washed and dried.

The granules obtained exhibited a mean particle diameter of 1.5 mm.

Coating and processing correspond to points 1b) and 1c).

EXAMPLE 3

Polymerization

A mixture of 150 parts of water, 0.1 part of sodium pyrophosphate, 100 parts of styrene, 0.15 part of benzoyl peroxide and 0.25 part of t-butyl perbenzoate (as polymerization initiators), and 0.005 part of the chain-transfer agent tert-dodecyl mercaptan was heated to 85°C over the course of 90 minutes with stirring in a pressure-tight stirred reactor made from stainless steel. The temperature was subsequently increased continuously to 125°C over the course of 3.5 hours. After 2 hours from 85°C, 2 parts of a 10 % strength aqueous solution of polyvinylpyrrolidone were added. After 3 hours from 85°C, 7 parts of pentane were metered into the stirred reactor. The mixture was then stirred at 120°C for a further 5 hours. The conversion was 35 % when 125°C had been

reached and 85 % when the maximum temperature of 125°C had been reached. After 5 hours at 125°C, the polymer only had a styrene content of 0.09 %. The batch was subsequently cooled, and the polymer was separated off, washed and dried.

The granules obtained exhibited a mean particle diameter of 1.5 mm.

Coating and processing correspond to points 1b) and 1c).

EXAMPLE 4

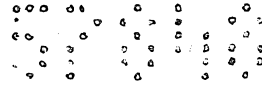
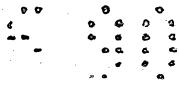
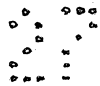
The procedure was as in Example 2, but 0.005 part of the chain-transfer agent tert-dodecyl mercaptan was added as a substance which further improves the expandability. The conversion was 32 % when 100°C had been reached and 82 % when 120°C had been reached. The styrene content of the polymer was 0.1 %.

Coating and processing correspond to points 1b) and 1c).

EXAMPLE 5 (Comparisons)

The mixtures as per Examples 1 (Example 5.1) and 2 (Example 5.2) were heated to 85°C over the course of 3 hours with stirring in a pressure-tight stirred reactor made from stainless steel. The temperature was subsequently increased continuously to 120°C over the course of 5 hours. Otherwise, the procedure of Example 1 was followed.

Coating and processing correspond to points 1b) and 1c).



Table

	Expandability as throughput (at a bulk density of 15 g/l)	Expandability as the minimum bulk density achievable after 6 minutes pre-foaming in flowing steam (1 bar abs.) in a Rauscher box	Melt extensibility μ	Reversible elongation E_r
	kg/h	g/cm ³	Pas	
Example 1	140	0.0105	$2.3 \cdot 10^6$	0.8
Example 2	137	0.011	$2.4 \cdot 10^6$	0.82
Example 3	145	0.010	$2.9 \cdot 10^6$	0.85
Example 4	145	0.010	$2.6 \cdot 10^6$	0.79
Example 5.1 as comparison	105	0.012	$5.6 \cdot 10^6$	1.1
Example 5.2 as comparison	110	0.0125	$4.2 \cdot 10^6$	1.0

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the preparation of a bead-form expandable styrene polymer by polymerization of styrene, if desired with further comonomers, in aqueous suspension in the presence of customary suspension stabilizers and customary styrene-soluble polymerization catalysts and with addition of from 1 to 10% by weight of a C₃- to C₆- hydrocarbon as blowing agent and, if desired, customary additives in effective amounts, which comprises

- a) initiating the polymerization by rapidly heating the polymerizing batch to from 80 to 90°C within a maximum of 2 hours,
- b) subsequently allowing the reaction temperature to increase to from 120°C to 130°C by from 8 to 17°C per hour, and wherein
- c) the conversion is from 30 to 60% when 100°C is reached, and
- d) the conversion is 80% or more when the maximum temperature is reached, and which comprises
- e) subsequently keeping the batch at from 100 to 130°C until the residual monomer content in the polymer has dropped to less than 0.1%.

2. A process as claimed in claim 1, wherein the polymerization is carried out in the presence of a customary chain-transfer agent, in particular tert-dodecyl mercaptan, in an amount of from 0.0001 to 0.01% by weight, based on styrene.

3. Foam mouldings having a density of from 0.005 to 0.1g/cm³, characterised in that said foam mouldings are made of expandable styrene polymer produced in accordance with the process of claim 1 or claim 2.

4. A process for the preparation of a bead-form expandable styrene, substantially as hereinbefore described with reference to the Examples.

DATED this 26th day of June 1990.

BASF AKTIENGESELLSCHAFT

WATERMARK PATENT & TRADEMARK ATTORNEYS
HAWTHORN VIC 3122

