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METHOD FOR INHIBITING POPCORN POLYMER FORMATION BY HEAT
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- (71) Applicant(s)
EXXON CHEMICAL PATENTS INC.
- (72) Inventor(s)
HSIANG-NING SUN; CYNTHIA CHILDRE INGRAM; JOHN JOSEPH MCMANUS JR.
- (74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122
- (56) Prior Art Documents
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(57) This invention relates to the use of heat to inhibit popcorn polymer formation. For purposes of this application, the term "popcorn polymer" is understood to include popcorn polymer seeds and deposits.

The term "inhibit" is understood to encompass all degrees of adversely affecting the formulation of popcorn polymer - e.g., both slowing as well as completely halting popcorn polymer growth.

Claim

1. A method for inhibiting the growth of popcorn polymer, consisting essentially of treatment of said popcorn polymer with heat.
2. The method of claim 1, wherein said treatment is conducted in the substantial absence of organic material from which said popcorn polymer is formed.
3. The method of claim 1, wherein said treatment is conducted at a temperature of between 60°C and 650°C, and for a period of between 15 minutes and 100 hours.

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11. A method for inhibiting the growth of popcorn polymer, comprising treatment of said popcorn polymer with heat and with at least one chemical inhibitor of popcorn polymerization, in the substantial absence of organic material from which said popcorn polymer is formed.

20. A method for inhibiting the growth of popcorn polymer, comprising treatment of said popcorn polymer with heat, at a temperature of between 60°C and 260°C, for a period of time sufficient to inhibit the growth of said popcorn polymer.

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(71) Applicant: EXXON CHEMICAL PATENTS INC. [US/US]; 1900 East Linden Avenue, Linden, NJ 07036-0710 (US).

(72) Inventors: SUN, Hsiang-ning ; 4212 Villanova, Houston, TX 77005 (US). INGRAM, Cynthia, Childre ; 1011 Maywood Drive, Denham Spring, LA 70726 (US). MCMANUS, John, Joseph, Jr. ; 12340 East Milburn Drive, Baton Rouge, LA 70815 (US).

(74) Agents: SHERER, Edward, F. et al.; Exxon Chemical Company, 5200 Bayway Drive, Baytown, TX 77520-5200 (US).

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(54) Title: METHOD FOR INHIBITING POPCORN POLYMER FORMATION BY HEAT

(57) Abstract

Inhibition of popcorn polymer growth by treatment with heat. Heat can be applied to extant popcorn polymer, particularly in the absence of organic material from which the popcorn polymer is formed. A chemical inhibitor of popcorn polymerization can be used in conjunction with the heat treatment.

METHOD FOR INHIBITING POPCORN POLYMER FORMATION BY HEAT

CONCURRENTLY FILED APPLICATIONS

Concurrently with this application, also filed were applications entitled INHIBITING POPCORN POLYMER FORMATION WITH MERCAPTANS, Australian Application No. 14115/92; INHIBITING POPCORN POLYMER FORMATION WITH COMPOUNDS INCORPORATING GROUP IV ELEMENTS, Australian Application No. 88507/91; INHIBITING POPCORN POLYMER FORMATION WITH ESTERS OF INORGANIC ACIDS, Australian Application No. 12761/92; and INHIBITING POPCORN POLYMER FORMATION WITH ALKYL HALIDES, Australian Application No. 12750/92. These applications are all incorporated herein in their entireties, by reference thereto.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is directed to preventing further growth of popcorn polymer seeds or deposits. The desired result is effected by treatment of the popcorn polymer with sufficient heat to inhibit, i.e., to prevent, retard, or stop popcorn polymer growth.

One aspect of the invention pertains to such heat treatment of popcorn polymer in the absence, or substantial absence, of organic material from which the popcorn polymer is formed. Another aspect of the invention pertains to such heat treatment of popcorn polymer, wherein the heat treatment is the sole, or essentially the sole, means for effecting the inhibition, retardation, or cessation of popcorn polymer growth.

2. Description of Background and Other Information

Popcorn polymers are known to form from all manner of organic material, particularly olefinically unsaturated monomers, including olefins and diolefins; especially susceptible are the conjugated diolefins, e.g., butadiene and isoprene, and vinyl compounds, e.g. styrenes and acrylates.

Known as popcorn polymers because they resemble popped corn, these polymers are also referred to in the art as sponge polymers, granular polymers, cauliflower-like polymers, nodular polymers, fluffy polymers, proliferous polymers, and crusty polymers.

Popcorn polymer has been considered to occur from spontaneous monomer polymerization. It can occur in both liquid phase and vapor phase, and at any stage of use or handling of the monomer, e.g., recovery, separation, manufacturing, purification, storage, etc. High concentrations of monomer are particularly advantageous for its formation.

Specifically, it appears that the presence of one or more initiators - e.g., water, oxygen, hydrogen, peroxide - results in the formation of popcorn polymer "seeds" in the organic material. The seeds themselves then perpetuate polymerization, without further requiring an initiator and/or a crosslinking agent; they serve as sites for further polymerization.

As the particular mechanism, it is believed that monomer diffuses through the surface of the growing polymer mass, and is added to the polymer at the center thereof. For this reason, such polymerization is referred to as occurring "from the inside out."

Consequently, there is continued incorporation of monomer into the polymer phase, leading to buildup of the popcorn polymer. The result is a hard polymeric foulant, which can cause serious equipment and safety concerns if left unchecked.

A particular problem attendant upon popcorn polymer formation is its extreme resistance to deactivation, once present in a system. Some of the seeds become attached to the processing and handling equipment, and cannot be readily removed by mechanical means; moreover, being insoluble in most

common solvents, they are virtually impossible to wash out by use of such solvents.

Even after equipment and storage facilities have been cleaned thoroughly, residual particles of popcorn polymer remain, and promote unwanted polymer growth. Trace particles remaining in the equipment will stay active for long periods without the presence of monomer, and serve to initiate polymerization when once again contacted therewith.

Different inhibitors are known for use against popcorn polymer formation. Examples of these are the following: t-butylcatechol; sodium nitrite, as disclosed in LIU, "Plugging-Up of Equipment by Self-Polymerization Butadiene Production and Its Prevention," China Synthetic Rubber Industry, 11(5) 357-360 (1988); carbon disulfide and elemental phosphorous, as disclosed in HASKELL, U.S. Patent No. 4,404,413, which also refers to hydrogen sulfide, to ethane-, propane-, and hexane-thiol, and to ethyl disulfide as being known in the prior art; N,N-dialkylhydroxylamines, as disclosed in TOKAI ELECTRO-CHEMICAL CO., Japanese Kokai No. 66,223,003, as well as in LIU et al., "Determination of Traces of Diethylhydroxylamine Inhibitor in C₅ Fraction by Gas Chromatography," China Synthetic Rubber Industry, 12(6), 408-410 (1989), and in ALBERT, U.S. Patent No. 3,148,225, the latter of these also referring to nitrites, nitroso compounds, NO₂, N₂O₃, phenolic compounds, sulfur, aromatic amines, and hydroxylamine as being known in the prior art; trialkylamine oxides, as also disclosed in TOKAI ELECTRO-CHEMICAL CO.; N-hydroxymorpholine, used in conjunction with N,N-dialkylhydroxylamines, as disclosed in CASE et al., U.S. Patent No. 3,265,752, or in conjunction with N-hydroxypiperidine, as disclosed in MccOY et al., U.S. Patent No. 3,265,751; adducts of phenols and hydroxylamines, as disclosed in ALBERT et al., U.S. Patent No. 3,493,063; reaction products of nitrous acid and 1,3-

dichlorobutene-2 or diisobutylene, as disclosed in BENJAMINS, U.S. Patent No. 3,560,577, which also refers to nitrogen dioxide, the addition product of 1,3-dichloro-2-butene and nitrogen dioxide, and ion-exchange resin containing nitrite ions, as being known in the prior art; butyraldoxime, as disclosed in KEOWN, U.S. Patent No. 3,560,577; and nitrogen tetroxide-diisobutylene addition products, as disclosed in COLBERT, U.S. Patent No. 3,175,012.

Those inhibitors known in the prior art are generally effective in stopping the formation of popcorn polymer seeds, when admixed with popcorn polymer-forming material; however, they are only minimally effective in stopping the growth of seeds already in existence. Further, such inhibitors which are relatively heavy will work in liquid phase, but are of little or no use in vapor phase, because in this state their weight hinders their distribution.

It has been discovered that a simpler and easier way to inhibit popcorn polymer formation is by exposing extant popcorn polymer, e.g., in the form of seeds, deposits, or other sources, to heat. Such heat treatment has unexpectedly been found to "kill" popcorn polymer seeds or sources already formed, i.e., to halt their growth, or at least to retard their growth.

As previously discussed, the chemical inhibitors previously known in the art are not effective for treatment of popcorn polymer already in being, but have significant utility only for preventing the organic material from forming popcorn polymer. Accordingly, in contrast with such inhibitors, the heat treatment of the invention can be used to treat popcorn polymer seeds in the absence of the seed-forming organic material, i.e., by exposing such seeds to heat; in this manner, popcorn polymer formation can be

controlled without the necessity for continuous addition of chemical inhibitors to the organic material.

SUMMARY OF THE INVENTION

5 According to the invention, popcorn polymer is treated with heat to inhibit growth thereof. Specifically, the treatment utilizes a sufficient amount of heat, for a sufficient period of time, to effect the inhibition.

10 In one embodiment, the process of the invention consists essentially of treating popcorn polymer with heat. In another embodiment, the process of the invention comprises treatment of popcorn polymer with heat, in the absence, or substantial absence, of organic material from which the popcorn polymer is formed. Preferably, the process of the invention consists essentially of treating popcorn polymer with heat, and is also
15 conducted in the absence, or substantial absence, of popcorn polymer-forming organic material.

Different ranges of temperatures and periods of treatment are suitable for the process of the invention. Encompassed within the scope of the invention is treatment of popcorn
20 polymer at a temperature of between 60°C. and 650°C., and for a period of between 15 minutes and 100 hours. More preferably, the popcorn polymer is treated at a temperature of between 120°C. and 430°C., and for a period of between 30 minutes and 48 hours.

25 The treatment may be conducted at a temperature of 350°C. or greater, for a period of time sufficient to inhibit the growth of the popcorn polymer. In the alternative, the treatment may be conducted at a temperature of 400°C. or greater.

30 Where the popcorn polymer is formed from 1,3-butadiene, the process of the invention is preferably conducted at a temperature of at least 260°C., and for a period of at least 24 hours. This treatment is preferably conducted in the

absence, or at least substantial absence, of the 1,3-butadiene starting material.

DETAILED DESCRIPTION OF THE INVENTION

5 This invention relates to the use of heat to inhibit popcorn polymer formation. For purposes of this application, the term "inhibit" is understood to encompass all degrees of adversely affecting the formulation of popcorn polymer - e.g., both slowing as well as completely halting popcorn polymer growth.

10 Encompassed within the scope of the invention is heat treatment of any popcorn polymer formed from organic material; the term "organic material" encompasses any organic material in which popcorn polymer forms. Such organic material includes, but is not limited to, olefins and diolefins, particularly the conjugated diolefins, as well as the vinyl
15 compounds, as discussed in HASKELL, U.S. Patent No. 4,404,413; this patent is incorporated herein in its entirety, by reference thereto.

20 Specifically, suitable such organic material includes monovinyl compounds such as styrene, acrylic acid and its esters, such as methylacrylate, ethylacrylate, and butylacrylate; methacrylates such as methyl methacrylate, ketones such as methyl vinyl ketone, and nitriles such as acrylonitrile. Appropriate divinyl compounds include 1,3-
25 butadiene, isoprene, dimethyl-2,3-butadiene, chloroprene, and bromoprene.

Further as to the organic material, two or more monomers such as any combination of those discussed above, can be inhibited from forming popcorn polymer by treating the popcorn
30 polymer formed from any such combination according to the invention.

While retaining its ordinary meaning in the art, i.e., as the starting unit for polymerization, the term "monomer",

absence, or at least substantial absence, of the 1,3-butadiene starting material.

DETAILED DESCRIPTION OF THE INVENTION

This invention relates to the use of heat to inhibit popcorn polymer formation. For purposes of this application, the term "popcorn polymer" is
5 understood to include popcorn polymer seeds and deposits.

The term "inhibit" is understood to encompass all degrees of adversely affecting the formulation of popcorn polymer - e.g., both slowing as well as completely halting popcorn polymer growth.



as used herein, is further understood to encompass all organic material wherein is formed the popcorn polymer susceptible to heat treatment in accordance with the invention. The process of the invention encompasses exposure of popcorn polymer to sufficient heat, in the presence, absence, or substantial absence of monomer, in any manner which will inhibit, prevent, retard, or stop the growth of such popcorn polymer, or the formation of popcorn polymer.

A particular advantage of the process of the instant invention is that, as indicated, it may be conducted whether or not the monomer from which popcorn polymer is formed is present. In a preferred embodiment of the invention, heat treatment of the popcorn polymer is effected in absence, or substantial absence, of any other means for inhibiting popcorn polymer growth, such as chemical inhibitors.

In accordance with the invention, popcorn polymers are inhibited from forming in an organic polymer starting material by exposing popcorn polymer to heat. The degree of heat applied should be sufficient to inhibit popcorn polymer growth-specifically, sufficient to inhibit the further growth of popcorn polymer exposed to such heat.

Temperatures of about 60°C. to about 650°C. are effective in inhibiting popcorn polymer formation. Preferred temperatures range from about 120°C. to about 430°C.; most preferred are temperatures of 260°C. and above.

The heat should be applied to the popcorn polymer for a period sufficient to inhibit popcorn polymer growth; specifically, sufficient to inhibit the further growth of popcorn polymer so treated.

The time for which the popcorn polymer may be heated at the indicated temperatures may vary widely; times ranging from 1 minute to several weeks may be acceptable. Periods of 15 minutes to 100 hours are preferred, with a range of 30 minutes

to 48 hours being more preferred.

The heat required to raise the temperature to the required level can be generated by any means which are considered acceptable to one of ordinary skill in the art. This is conveniently accomplished by simply heating the popcorn polymer with an external heat source, or by passing a heated gas through the system containing popcorn polymer to be deactivated.

The methods are not limited to any particular gaseous atmosphere. The atmosphere in which the method is practiced can be air, nitrogen, oxygen-containing gas, helium, argon, steam, and any other gaseous atmospheres standardly used in dealing with organic polymer starting materials, and mixtures thereof.

Similarly, extensive variations are appropriate for the pressure under which the popcorn polymer is treated. For example, the pressure exerted can range from high vacuum (> 0.0001 atm.) to superatmospheric pressure (\leq 1000 atm.). Essentially, any pressure is suitable which can be tolerated by the equipment with which, or wherein, the process of the invention is conducted.

In a particularly preferred embodiment, the monomer to be treated is heated to a temperature of approximately 260°C., or greater, for a period of approximately 24 hours or longer. Such treatment essentially deactivates the popcorn polymer, and produces long lasting inhibition of popcorn polymer formation when the treated popcorn polymer is exposed to polymerizable monomer. Most preferably, no chemical inhibitor is employed in this embodiment of the process of the invention.

Preferably, heat treatment of popcorn polymer, in accordance with the process of the invention, is conducted in the absence of the organic material from which the popcorn

polymer is formed; also as a preferred embodiment, such treatment is conducted without the presence of any other means for inhibiting popcorn polymer formation - e.g., chemical inhibitors of popcorn polymerization, as previously discussed. 5 However, the presence of such organic material, or such other means of inhibition, or both, in addition to heat treatment, is within the scope of this invention.

Where the process of the invention incorporates use of chemical inhibitors as well as exposure of popcorn polymer to heat, any such chemical inhibitors having utility for 10 inhibiting popcorn polymer formation, when used in this manner, are suitable; these may be employed in the minimum amount required for inhibiting popcorn polymer growth, as may be ascertained by one skilled in the art. Included are all 15 such chemical inhibitors as disclosed in the co-pending applications discussed at the beginning of this application, and all such chemical inhibitors disclosed in the patents and other publications cited herein, all of these patents and other publications being incorporated herein in their 20 entireties, by reference thereto.

Generally, such parameters as temperature, time, and pressure will vary in accordance with a variety of factors. These may include, but are not limited to, the amount of popcorn polymer present, its growth rate in the presence of 25 monomer, whether such monomer is present or absent during treatment in accordance with the process of the invention, the effectiveness of any additional chemical inhibitor (if any is present), etc. These values are readily ascertainable to one of ordinary skill in the art.

30 The process of the invention is suitable for treating all systems and other equipment for the manufacture, use, storage, or any other type of handling of popcorn polymer-forming organic material, for the purpose of inhibiting growth

of popcorn polymer seeds or other deposits residing therein. For instance, appropriate systems include those for separating desired monomer from a mixed hydrocarbon stream, and those for conducting chemical reactions utilizing the monomer; monomer storage equipment, e.g., tanks, may also be treated in accordance with the process of the invention.

In order to illustrate more fully the nature of the present invention and the manner of practicing the same, but not by way of limitation, the following experimental procedure is presented.

EXPERIMENTAL PROCEDURE

This experimental procedure involved initially treating popcorn polymer seeds, derived from 1,3-butadiene, in accordance with the process of the invention, then leaving the seeds in the presence of butadiene. As a control, this procedure also included a 1,3-butadiene seed/monomer system without such prior treatment.

Specifically, in each test according to this procedure except the control, the seed was placed in an oven in an atmosphere of ambient air. Therein, the seed was subjected to a specified temperature, at a specific pressure, for a specified period of time.

The seeds thusly treated, and the control seed, were suspended in glass polymerization vessels. All air was removed from these vessels, either by evacuation, or by flushing with nitrogen, and 1,3-butadiene was condensed into the vessel at -78°C. In this manner, gas phase polymerization was utilized for all the tests, including the control - i.e., being suspended in their respective vessels, the seeds were maintained out of contact with 1,3-butadiene liquid.

In each test, the system thus established was maintained at 60°C., as a static system, and at autogenic pressure. Popcorn polymer growth rates were measured according to the

growth rate of the control.

Specifically, the amount of growth obtained from the control was arbitrarily designated as 1.0. Growth of the other seeds was measured according to this standard.

5 The results of this procedure are set forth in the Table.

TABLE

| | Heat Treatment Temperature (C.) | Heat Treatment Pressure (mmHg.) | Heat Treatment Period (hours) | Monomer Treatment Period (days) | Popcorn Polymer Growth Rate |
|----|------------------------------------|------------------------------------|----------------------------------|------------------------------------|--------------------------------|
| | Control (no heat treatment) | - | - | 14 | 1.0 |
| 15 | 25 | 746 | 48 | 14 | 1.2 |
| | 25 | 746 | 48 | 14 | 0.9 |
| | 90 | 760 | 24 | 14 | 0.25 |
| | 90 | 760 | 24 | 14 | 0.22 |
| | 150 | 760 | 24 | 14 | 0.10 |
| 20 | 150 | 760 | 24 | 14 | 0.15 |
| | 260 | 760 | 24 | 65 | 0.0 |
| | 260 | 760 | 24 | 65 | 0.0 |

For the two seeds heated only to 25°C., there was little difference between their growth rates and that of the control (untreated) seed. In contrast, significant growth rate reductions were observed for the seeds treated at higher temperatures.

The growth rates of the two seeds subjected to 90°C. were 0.25 and 0.22, in comparison with the arbitrarily designated standard rate of 1.0 for the control. These results signify a 75% reduction in popcorn polymer growth rate for the two seeds so treated.

A yet greater reduction in growth rate occurred for the seeds subjected to 150°C. By the same comparison, the growth rates for these two examples were 0.1 and 0.15, equating to approximately a 90% to 95% reduction.

Heating at yet higher temperatures resulted in further improvement; no growth occurred for the two seeds treated at 260°C. This complete inhibition was observed even after 65 days, more than four times as long as the exposure of the other seeds in the procedure to butadiene.

Accordingly, the higher the temperature to which the seeds were exposed, the lower their growth rates in the presence of monomer. Where temperatures were sufficiently high, popcorn polymer growth was completely halted.

Finally, although the invention has, as been noted above, been described with reference to particular means, materials and embodiments, it should be noted that the invention is not limited to the particulars disclosed, and extends to all equivalents within the scope of the claims. The above description and examples are merely illustrative; numerous changes and variations may be made without departing from the spirit and scope of the invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method for inhibiting the growth of popcorn polymer, consisting essentially of treatment of said popcorn polymer with heat.
2. The method of claim 1, wherein said treatment is conducted in the substantial absence of organic material from which said popcorn polymer is formed.
3. The method of claim 1, wherein said treatment is conducted at a temperature of between 60°C and 650°C, and for a period of between 15 minutes and 100 hours.
4. The method of claim 3, wherein said treatment is conducted at a temperature of between 120°C and 430°C, and for a period of between 30 minutes and 48 hours.
5. The method of claim 1, wherein said treatment is conducted at a temperature of at least about 350°C, for a period of time sufficient to inhibit the growth of said popcorn polymer.
6. The method claim 5, wherein said treatment is conducted at a temperature of at least about 400°C, for a period of time sufficient to inhibit the growth of said popcorn polymer.
7. The method of claim 1, wherein said popcorn polymer is formed from 1,3-butadiene, and wherein said treatment is conducted at a temperature of at least about 260°C, and for a period of at least about 24 hours.
8. The method of claim 7, wherein said treatment is conducted in the substantial absence of 1,3-butadiene.

9. The method of claim 1, wherein said popcorn polymer is formed from isoprene, and wherein said treatment is conducted at a temperature of at least about 260°C, and for a period of at least about 24 hours.

10. The method of claim 9, wherein said treatment is conducted in the substantial absence of isoprene.

11. A method for inhibiting the growth of popcorn polymer, comprising treatment of said popcorn polymer with heat and with at least one chemical inhibitor of popcorn polymerization, in the substantial absence of organic material from which said popcorn polymer is formed.

12. The method of claim 11, wherein said treatment is conducted at a temperature of between 60°C and 650°C, and for a period of between 15 minutes and 100 hours.

13. The method of claim 12, wherein said treatment is conducted at a temperature of between 120°C and 430°C, and for a period of between 30 minutes and 48 hours.

14. The method of claim 11, wherein said treatment is conducted at a temperature of at least about 350°C, for a period time sufficient to inhibit the growth of said popcorn polymer.

15. The method of claim 14, wherein said treatment is conducted at a temperature of at least about 400°C, for a period of time sufficient to inhibit the growth of said popcorn polymer.

16. The method of claim 11, wherein said popcorn polymer is formed from 1,3-butadiene, and wherein said treatment is conducted at a temperature of at least about 260°C, and for a period of at least about 24 hours.

17. The method of claim 16, wherein said treatment is conducted in the substantial absence of 1,3-butadiene.

18. The method of claim 11, wherein said popcorn polymer is formed from isoprene, and wherein said treatment is conducted at a temperature of at least about 260°C, and for a period of at least about 24 hours.


19. The method of claim 18, wherein said treatment is conducted in the substantial absence of isoprene.

20. A method for inhibiting the growth of popcorn polymer, comprising treatment of said popcorn polymer with heat, at a temperature of between 60°C and 260°C, for a period of time sufficient to inhibit the growth of said popcorn polymer.

21. A method for inhibiting the growth of popcorn polymer, comprising treatment of said popcorn polymer with heat, at a temperature of between 60°C and 150°C, for a period time sufficient to inhibit the growth of said popcorn polymer.

DATED this 24th day of November, 1995

EXXON CHEMICAL PATENTS, INC.



WATERMARK PATENT & TRADEMARK ATTORNEYS
290 BURWOOD ROAD
HAWTHORN VICTORIA 3122
AUSTRALIA

(DOC 03 AU1324292.WPC LPS/MED:KP)

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 92/00609

| I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁴ According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : C 08 F 6/26 | | | | | | | | | | | |
|---|--|-------------------------------------|--|--|---|--|--|-------------|---|---|--------------|
| II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Minimum Documentation Searched ⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 30%; border-bottom: 1px solid black;">Classification System </td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="padding: 5px;">IPC⁵ </td> <td style="padding: 5px;">C 08 F 6/00, C 08 F 12/00, C 08 F 36/00</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black; margin: 5px 0;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸</div> | | | Classification System | Classification Symbols | IPC ⁵ | C 08 F 6/00, C 08 F 12/00, C 08 F 36/00 | | | | | |
| Classification System | Classification Symbols | | | | | | | | | | |
| IPC ⁵ | C 08 F 6/00, C 08 F 12/00, C 08 F 36/00 | | | | | | | | | | |
| III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹ <table border="1" style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <thead> <tr> <th style="width: 10%; border: none;">Category ¹⁰</th> <th style="width: 70%; border: none;">Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²</th> <th style="width: 20%; border: none;">Relevant to Claim No. ¹³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top; border: none;">X</td> <td style="border: none;"> ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING, vol. 13, 1988, JOHN WILEY & SONS, New York, S. YAMAMOTO et al. "Proliferous polymerization", see pages 453-463; especially page 454, lines 23-31; page 455, lines 26-29. --- </td> <td style="text-align: center; vertical-align: top; border: none;">1, 3, 8, 11</td> </tr> <tr> <td style="text-align: center; vertical-align: top; border: none;">X</td> <td style="border: none;"> DD, B, 129 560 (VEB CHEMISCHE WERKE BUNA) 25 January 1978 (25.01.78), see claim; examples. ----- </td> <td style="text-align: center; vertical-align: top; border: none;">1, 3, 10, 11</td> </tr> </tbody> </table> | | | Category ¹⁰ | Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹² | Relevant to Claim No. ¹³ | X | ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING, vol. 13, 1988, JOHN WILEY & SONS, New York, S. YAMAMOTO et al. "Proliferous polymerization", see pages 453-463; especially page 454, lines 23-31; page 455, lines 26-29. --- | 1, 3, 8, 11 | X | DD, B, 129 560 (VEB CHEMISCHE WERKE BUNA) 25 January 1978 (25.01.78), see claim; examples. ----- | 1, 3, 10, 11 |
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| X | ENCYCLOPEDIA OF POLYMER SCIENCE AND ENGINEERING, vol. 13, 1988, JOHN WILEY & SONS, New York, S. YAMAMOTO et al. "Proliferous polymerization", see pages 453-463; especially page 454, lines 23-31; page 455, lines 26-29. --- | 1, 3, 8, 11 | | | | | | | | | |
| X | DD, B, 129 560 (VEB CHEMISCHE WERKE BUNA) 25 January 1978 (25.01.78), see claim; examples. ----- | 1, 3, 10, 11 | | | | | | | | | |
| <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%; vertical-align: top; border: none;"> ¹⁴ Special categories of cited documents: ¹⁴ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" documents which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td style="width: 50%; vertical-align: top; border: none;"> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family </td> </tr> </table> | | | ¹⁴ Special categories of cited documents: ¹⁴ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" documents which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family | | | | | | | |
| ¹⁴ Special categories of cited documents: ¹⁴ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" documents which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed | "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "Z" document member of the same patent family | | | | | | | | | | |
| IV. CERTIFICATION <table style="width: 100%; border-collapse: collapse; margin-top: 5px;"> <tr> <td style="width: 50%; border: none;"> Date of the Actual Completion of the International Search <div style="text-align: center; font-size: 1.2em;">15 May 1992</div> </td> <td style="width: 50%; border: none;"> Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">16. 06. 92</div> </td> </tr> <tr> <td style="border: none;"> International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> </td> <td style="border: none;"> Signature of Authorized Officer <div style="text-align: center;"> TORIBIO </div> </td> </tr> </table> | | | Date of the Actual Completion of the International Search <div style="text-align: center; font-size: 1.2em;">15 May 1992</div> | Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">16. 06. 92</div> | International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> | Signature of Authorized Officer <div style="text-align: center;"> TORIBIO </div> | | | | | |
| Date of the Actual Completion of the International Search <div style="text-align: center; font-size: 1.2em;">15 May 1992</div> | Date of Mailing of this International Search Report <div style="text-align: center; font-size: 1.2em;">16. 06. 92</div> | | | | | | | | | | |
| International Searching Authority <div style="text-align: center; font-weight: bold;">EUROPEAN PATENT OFFICE</div> | Signature of Authorized Officer <div style="text-align: center;"> TORIBIO </div> | | | | | | | | | | |

ANHANG

ANNEX

ANNEXE

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

to the International Search
Report to the International Patent
Application No.

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/US 92/00609 SAE 56839

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentedokumente angegeben.
Diese Angaben dienen nur zur Unter-
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
in no way liable for these particulars
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of information.

La présente annexe indique les
membres de la famille de brevets
relatifs aux documents de brevets cités
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| In Recherchenbericht angeführtes Patentedokument Patent document cited in search report Document de brevet cité dans le rapport de recherche | Datum der Veröffentlichung Publication date Date de publication | Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets | Datum der Veröffentlichung Publication date Date de publication |
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| DD B 129560 | | keine - none - rien | |