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AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

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Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

[Continued on next page]

(54) Title: DEGRADABLE MATERIAL FOR DOWNHOLE APPLICATIONS

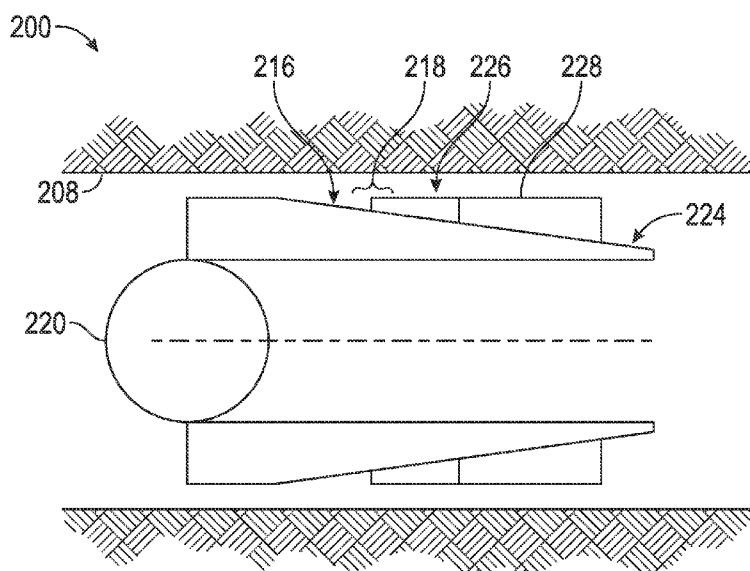


FIG. 2

(57) Abstract: In one aspect, degradable material is disclosed, including: a polyurethane component with a first degradation rate in a downhole environment; and a corrosive additive component with a second degradation rate that is higher than a first degradation rate in the downhole environment. In another aspect, a method of temporarily sealing a downhole zone is disclosed, including: providing a polyurethane component with a first degradation rate in a downhole environment; providing a corrosive additive component with a second degradation rate that is higher than a first degradation rate in the downhole environment; mixing the polyurethane component and the corrosive additive component to form a degradable material; sealing the downhole zone with the degradable material; exposing the degradable material to the downhole environment; and degrading the degradable material.

**Published:**

— *with international search report (Art. 21(3))*

## DEGRADABLE MATERIAL FOR DOWNHOLE APPLICATIONS

### **CROSS REFERENCE TO RELATED APPLICATIONS**

This application claims the benefit of U.S. Application No. 14/551976, filed on November 24, 2014, which is incorporated herein by reference in its entirety.

### **BACKGROUND**

#### **Field of the Disclosure**

[0001] This disclosure relates generally to controllably degradable materials and systems that utilize same for downhole applications.

#### **Background of the Art**

[0002] Wellbores are drilled in subsurface formations for the production of hydrocarbons (oil and gas). Hydrocarbons are trapped in various traps or zones in the subsurface formations at different depths. In order to facilitate the production of oil and gas, it is often desired to utilize fracturing operations. During fracturing operations, downhole plugs and corresponding seals are utilized to isolate zones to prevent and limit fluid flow. Such plugs and corresponding seals must be removed or otherwise destroyed before production operations can begin. Such removal operations may be costly and/or time consuming. It is desired to provide a material that can provide a downhole seal while providing desired and predictable degradable characteristics over a wide range of temperatures for the desired time of operations and applications.

[0003] The disclosure herein provides controlled degradable materials and systems using the same to withstand downhole conditions.

### **SUMMARY**

[0004] In one aspect, a degradable material is disclosed, including: a polyurethane component with a first degradation rate in a downhole environment; and a corrosive additive component with a second degradation rate that is higher than a first degradation rate in the downhole environment.

[0005] In another aspect, a method of temporarily sealing a downhole zone is disclosed, including: providing a polyurethane component with a first degradation rate in a downhole environment; providing a corrosive additive component with a second degradation rate that is higher than a first degradation rate in the downhole environment; mixing the polyurethane component and the corrosive additive component to form a degradable material;

sealing the downhole zone with the degradable material; exposing the degradable material to the downhole environment; and degrading the degradable material.

[0006] In another aspect, downhole system is disclosed, including: a casing string disposed in a wellbore; and a casing seal configured to seal against the casing string, including: a polyurethane component with a first degradation rate in a downhole environment; and a corrosive additive component with a second degradation rate that is higher than a first degradation rate in the downhole environment.

[0007] Examples of certain features of the apparatus and method disclosed herein are summarized rather broadly in order that the detailed description thereof that follows may be better understood. There are, of course, additional features of the apparatus and method disclosed hereinafter that will form the subject of the claims appended hereto.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

[0008] The disclosure herein is best understood with reference to the accompanying figures, wherein like numerals have generally been assigned to like elements and in which:

**FIG. 1** is a schematic diagram of an exemplary drilling system that includes downhole elements according to embodiments of the disclosure;

**FIG. 2** is a schematic diagram of an exemplary frac plug for use in a downhole system, such as the one shown in **FIG. 1**, according to one embodiment of the disclosure;

**FIG. 3** shows a view of an exemplary casing sealing member for use with the frac plug, such as the frac plug shown in **FIG. 2** for use with a downhole system, according to one embodiment of the disclosure;

**FIG. 3A** shows a view of another embodiment of a casing sealing member for use with the frac plug, such as the frac plug shown in **FIG. 2** for use with a downhole system, according to another embodiment of the disclosure;

**FIG. 4A** shows a chart representing the degradation characteristics of different polymeric resins at an exemplary downhole temperature;

**FIG. 4B** shows a chart representing the degradation characteristics of different polymeric resins at another exemplary downhole temperature;

**FIG. 4C** shows a chart representing the degradation characteristics of polymers with various corrosive filler at an exemplary downhole temperature; and

**FIG. 4D** shows a chart representing the degradation characteristics of polymers with various corrosive fillers at another exemplary downhole temperature.

## **DESCRIPTION OF THE EMBODIMENTS**

[0009] **FIG. 1** shows an exemplary embodiment of a downhole system for fracturing (or fracing) operations to facilitate the production of oil and gas. System **100** includes a wellbore **106** formed in formation **104** with casing **108** disposed therein.

[0010] In an exemplary embodiment, a wellbore **106** is drilled from a surface **102** to a downhole location **110**. Casing **108** may be disposed within wellbore **106** to facilitate production. In an exemplary embodiment, casing **108** is disposed through multiple zones of production **Z1...Zn** in a downhole location **110**. Wellbore **106** may be a vertical wellbore, a horizontal wellbore, a deviated wellbore or any other suitable type of wellbore or any combination thereof.

[0011] To facilitate fracturing operations, in an exemplary embodiment, frac plugs **116** are utilized within casing string **108**. In certain embodiments, frac plugs **116** are utilized in conjunction with casing seals **118** and frac balls **120** to isolate zones **Z1...Zn** for fracturing operations. In an exemplary embodiment, frac plugs **116** utilize casing seals **118** to seal plugs **116** against casing **108** of local zone **Z1** to prevent fluid flow therethrough. In certain embodiments, frac balls **120** are disposed at a downhole location **110** to obstruct and seal fluid flow in local zone **Z1** to facilitate flow to perforations **114**.

[0012] In an exemplary embodiment, frac fluid **124** is pumped from a frac fluid source **122** to a downhole location **110** to flow through perforations **114** in a zone **Z1** isolated by frac plug **116** and frac ball **120**. Advantageously, fracturing operations allow for more oil and gas available for production.

[0013] After fracturing operations, and before production operations, casing seals **118** are often removed or otherwise destroyed to allow the flow of oil and gas through casing **108**. In an exemplary embodiment, casing seals **118** are configured to seal against casing **108** of local zone **Z1** until a predetermined time at which casing seals **118** dissolve to facilitate the production of oil and gas. In various applications, downhole conditions may vary, causing degradation to occur at different rates. Advantageously, in an exemplary embodiment, the casing seals **118** herein are formed of two degradable materials to have predictable and adjustable degradation characteristics for various downhole temperature ranges.

[0014] **FIG. 2** shows a frac plug **216** for use downhole systems such as the system **100** shown in **FIG. 1** for fracturing operations. In an exemplary embodiment, frac plug system **200** includes frac plug **216** interfacing with casing **208** via casing seal **218** and slip **228** to create a seal to isolate a zone for fracturing operations. In certain embodiments, frac plug **216** further receives frac ball **220** to isolate frac fluid flow.

[0015] In an exemplary embodiment, casing seal **218** includes a wedge **224** and a casing sealing member **226**. In certain embodiments, wedge **224** is forced downhole to force casing sealing member **226** outward against casing **208** to seal against casing **208**. In certain embodiments, wedge **224** is forced via a setting tool, explosives, or any other suitable means. In certain embodiments, frac plug **216** further utilizes a slip **228** to position frac plug **216** with respect to casing **208** and further resist movement. Slip **228** may similarly be driven toward casing **208** via wedge **224**.

[0016] In an exemplary embodiment, casing sealing member **226** is formed of a degradable material. In an exemplary embodiment, the sealing member **226** is formed of two materials of different degradation rates for a given environment, to allow desired sealing characteristics while additionally allowing for the desired amount of degradation in varying downhole conditions. In downhole applications, downhole temperature may vary. In certain embodiments, the downhole temperature exposure to frac plug **216** varies from 100 to 350 degrees Fahrenheit at a particular downhole location for a given area. In certain embodiments, the temperature range of exposure may be larger or smaller. Typically, materials designed to degrade at a certain temperature may degrade too slowly or fail to degrade at a lower temperature, while at an elevated temperature, the material may degrade too quickly to perform desired functions. Advantageously, by utilizing casing sealing member **226** as described herein, a single frac plug **226** design may be utilized for various wells and well applications with a wide range of downhole temperatures, reducing costs and time compared to conventional solutions that may require a specially designed frac plug for a narrow temperature range.

[0017] **FIG. 3** shows an exemplary embodiment of casing sealing member **326**. In an exemplary embodiment, casing seal **326** includes a base material **330** and a secondary additive material **332**. In an exemplary embodiment, secondary additive material **332** is dispersed through base material **330** homogenously.

[0018] In an exemplary embodiment, base material **330** is a polymeric material. In an exemplary embodiment, base material **330** has a degradation rate that is contingent on the temperature of the fluid or environment in the wellbore. The base material **330** can include a polymer formed with isocyanates and a di-amine. In certain embodiments, the base material can include a polymer that includes TDI, MDI, PPDI, Polyether, polyether, polycaprolactone, and polycarbonates. The polymers may further include PC-PPDI, PC-MDI, PD-TDI, Ether-PPDI, Ether-MDI, Ether-TDI, Esther-PPDI, Ester-MDI, and Ester-TDI.

In an exemplary embodiment, base material **330** can be chosen due to the sensitivity to downhole conditions, degradation characteristics, and sealing characteristics.

[0019] **FIG. 4A** shows a chart of degradation characteristics of various polymeric resins exposed to 3.5 % salt water at an elevated temperature 250F, to simulate downhole conditions. The degradation is shown as weight lost over time. Certain types of resins degrade fast than other types of resins. In the chart shown, a temperature representing a relatively high downhole As shown in **FIG. 4A**, the type of polyurethane formation selected affects the degradation rate of the overall material, as certain polymers, such as CD220-4060 degrades much faster than the other resins shown. Advantageously, a polymer can be selected based on degradation characteristics.

[0020] **FIG. 4B** shows various polymeric resins at a lower temperature (150 F), wherein the resins degrade at a lower rate. Similarly, different polymers exhibit different degradation rates. In certain embodiments, certain polymers, such as CD220-7030, exhibit minimal % weight loss are relatively low temperatures. Accordingly, certain polymers may not dissolve within operating parameters at lower temperatures.

[0021] In an exemplary embodiment, insert material **332** is mixed with base material **330** to form a material with a desirable degradation characteristic. In an exemplary embodiment, insert material **332** is a corrodible material, such as a corrodible metal. In certain embodiments, the corrodible metal is a controlled electrolytic metallic (CEM) material, including, but not limited to, Intallic. In certain embodiments, insert material **332** is a corrodible powder that is readily mixed with base material **330**. In an exemplary embodiment, insert material **332** is a corrodible powder including, but not limited to adipic acid or citric acid.

[0022] **FIG. 4C** shows the effect of corrosive fillers and the relative faster degradation of an exemplary TDI-Ester polyurethane with corrosive fillers at 205 F. As shown by the chart, the addition of adipic acid or citric acid (at 28.6%) allows for a near linear degradation relationship over time. Accordingly, various corrosive fillers may be selected according to the desired degradation curve and time.

[0023] In certain embodiments, the relative amount of insert material **332** can be varied by weight or volume in relation to the base material **330**. **FIG. 4D** shows the effect of various amounts of corrosive fillers (citric acid). As shown by the series of degradation curves, the addition of citric acid allows for a controlled increase in degradation. Utilizing this relationship can allow for a degradable material to be adapted to a downhole temperature range to allow for adequate sealing performance and desired degradation characteristics.

[0024] FIG. 3A shows an alternative embodiment of a casing seal 326. In an exemplary embodiment, casing seal 326 includes a base material 330 and a meshed or interlinked material 332a. The meshed or interlinked material 332a may be formed of the same or similar corrodible materials as described above, and may ensure complete or at least adequate degradation. Degradation may occur to break the casing seal 326 into small chunks to allow more surface area to be exposed for greater degradation.

[0025] Therefore in one aspect, a degradable material is disclosed, including: a polyurethane component with a first degradation rate in a downhole environment; and a corrosive additive component with a second degradation rate that is higher than a first degradation rate in the downhole environment. In certain embodiments, the downhole environment has a temperature greater than 100 degrees Fahrenheit and less than 350 degrees Fahrenheit. In certain embodiments, the downhole environment includes a salt water content. In certain embodiments, the polyurethane component and the corrosive additive component are homogeneously mixed. In certain embodiments, the corrosive additive component is disposed in a mesh structure within the polyurethane component. In certain embodiments, the polyurethane component has a sealing characteristic. In certain embodiments, the polyurethane component includes: TDI, MDI, PPDI, polyether, polyester, polycaprolactone, and polycarbonate. In certain embodiments, the corrosive additive component includes a controlled electrolytic metallic, adipic acid, and citric acid.

[0026] In another aspect, a method of temporarily sealing a downhole zone is disclosed, including: providing a polyurethane component with a first degradation rate in a downhole environment; providing a corrosive additive component with a second degradation rate that is higher than a first degradation rate in the downhole environment; mixing the polyurethane component and the corrosive additive component to form a degradable material; sealing the downhole zone with the degradable material; exposing the degradable material to the downhole environment; and degrading the degradable material. In certain embodiments, the downhole environment has a temperature of at least 100 degrees Fahrenheit and no greater than 350 degrees Fahrenheit. In certain embodiments, the downhole environment includes a salt water content. In certain embodiments, further including mixing the polyurethane component and the corrosive additive component homogeneously. In certain embodiments, the corrosive additive component is disposed in a mesh structure within the polyurethane component. In certain embodiments, the polyurethane component has a sealing characteristic. In certain embodiments, the polyurethane component includes: TDI, MDI, PPDI, polyether, polyester, polycaprolactone, and polycarbonate. In certain embodiments,

the corrosive additive component includes a controlled electrolytic metallic, adipic acid, and citric acid.

[0027] In another aspect, a downhole system is disclosed, including: a casing string disposed in a wellbore; and a casing seal configured to seal against the casing string, including: a polyurethane component with a first degradation rate in a downhole environment; and a corrosive additive component with a second degradation rate that is higher than a first degradation rate in the downhole environment. In certain embodiments, the downhole environment has a temperature of at least 100 degrees Fahrenheit and no greater than 350 degrees Fahrenheit. In certain embodiments, the polyurethane component and the corrosive additive component are homogenously mixed. In certain embodiments, the corrosive additive component is disposed in a mesh structure within the polyurethane component.

[0028] The foregoing disclosure is directed to certain specific embodiments for ease of explanation. Various changes and modifications to such embodiments, however, will be apparent to those skilled in the art. It is intended that all such changes and modifications within the scope and spirit of the appended claims be embraced by the disclosure herein.

**CLAIMS**

1. A degradable material, characterized by:  
a polyurethane component (330) with a first degradation rate in a downhole environment; and  
a corrosive additive (332, 332a) component with a second degradation rate that is higher than a first degradation rate in the downhole environment.
2. The material of claim 1, wherein the downhole environment has a temperature between 100 degrees Fahrenheit and 350 degrees Fahrenheit.
3. The material of claim 1 or 2, wherein the downhole environment includes a salt water content.
4. The material of claim 1, wherein the polyurethane component and the corrosive additive component are homogenously mixed (FIG. 3).
5. The material of claim 1, wherein the corrosive additive component (332, 332a) is disposed in a mesh structure within the polyurethane component (FIG. 3A).
6. The material of any of claims 1-5, wherein the polyurethane component has a sealing characteristic.
7. The material of any of claims 1-6, wherein the corrosive additive component (332, 332a) includes one of: a controlled electrolytic metallic; an adipic acid; and a citric acid.
8. A method of temporarily sealing a downhole zone (Z1), characterized by:  
providing a polyurethane component (330) with a first degradation rate in a downhole environment (108);  
providing a corrosive additive component (332, 332a) with a second degradation rate that is higher than a first degradation rate in the downhole environment;  
mixing the polyurethane component and the corrosive additive component to form a degradable material (226);  
sealing the downhole zone with the degradable material (226);  
exposing the degradable material (226) to the downhole (108) environment; and  
degrading the degradable material (226) .
9. The method of claim 8, wherein the downhole environment (108) has a temperature of at least 100 degrees Fahrenheit and no greater than 350 degrees Fahrenheit.
10. The method of claim 8 or 9, wherein the downhole environment (108) includes a salt water content.

11. The method of claim 8, further comprising mixing the polyurethane component (330) and the corrosive additive component (332, 332a) homogenously (FIG. 3).

12. The method of claim 8, wherein the corrosive additive component (332, 332a) is disposed in a mesh structure within the polyurethane component (FIG. 3A).

13. The method of claim 8, wherein the corrosive additive component (332, 332a) includes one of: a controlled electrolytic metallic; an adipic acid; and a citric acid.

14. A downhole system, comprising:  
a casing string disposed in a wellbore; and  
a casing seal configured to seal against the casing string, including:  
a polyurethane component with a first degradation rate in a downhole environment;  
and  
a corrosive additive component with a second degradation rate that is higher than a first degradation rate in the downhole environment.

15. The system of claim 14, wherein the polyurethane component (330) and the corrosive additive component (332a) are homogenously mixed (FIG. 3) or the corrosive additive component is disposed in a mesh structure within the polyurethane component (FIG. 3A).

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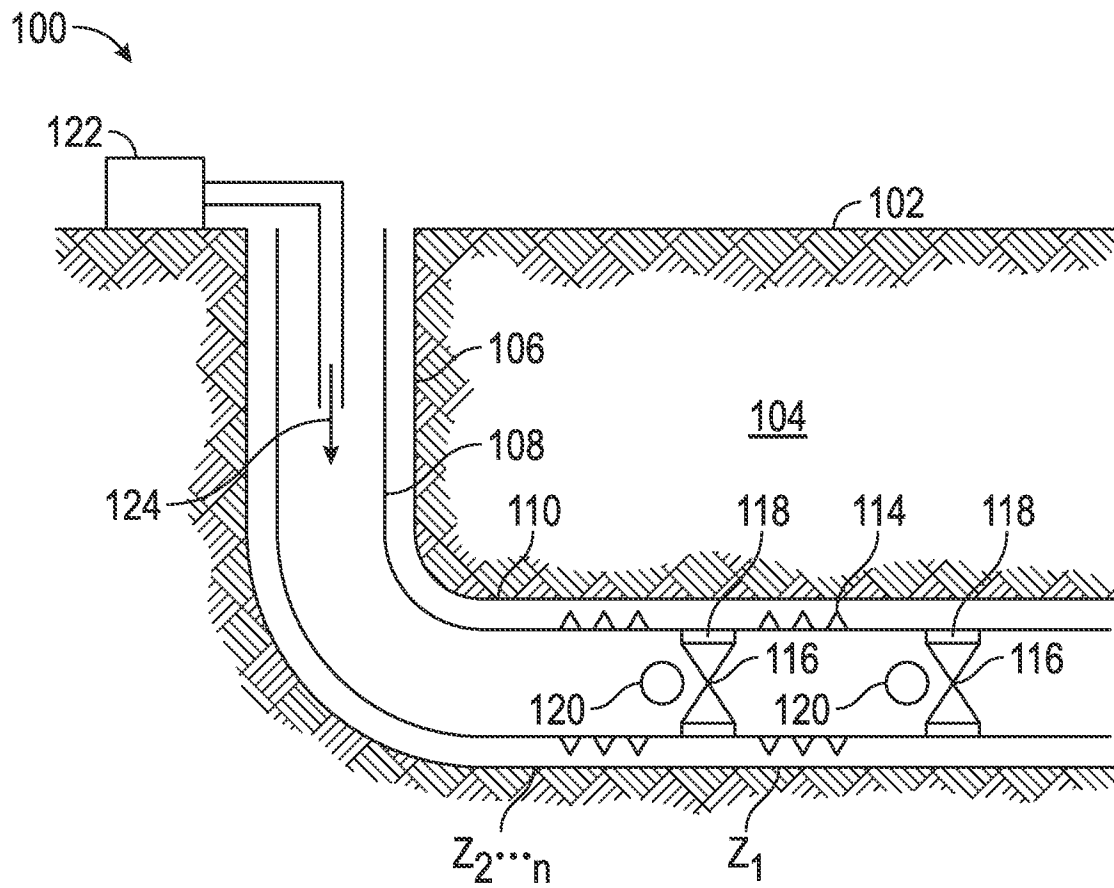


FIG. 1

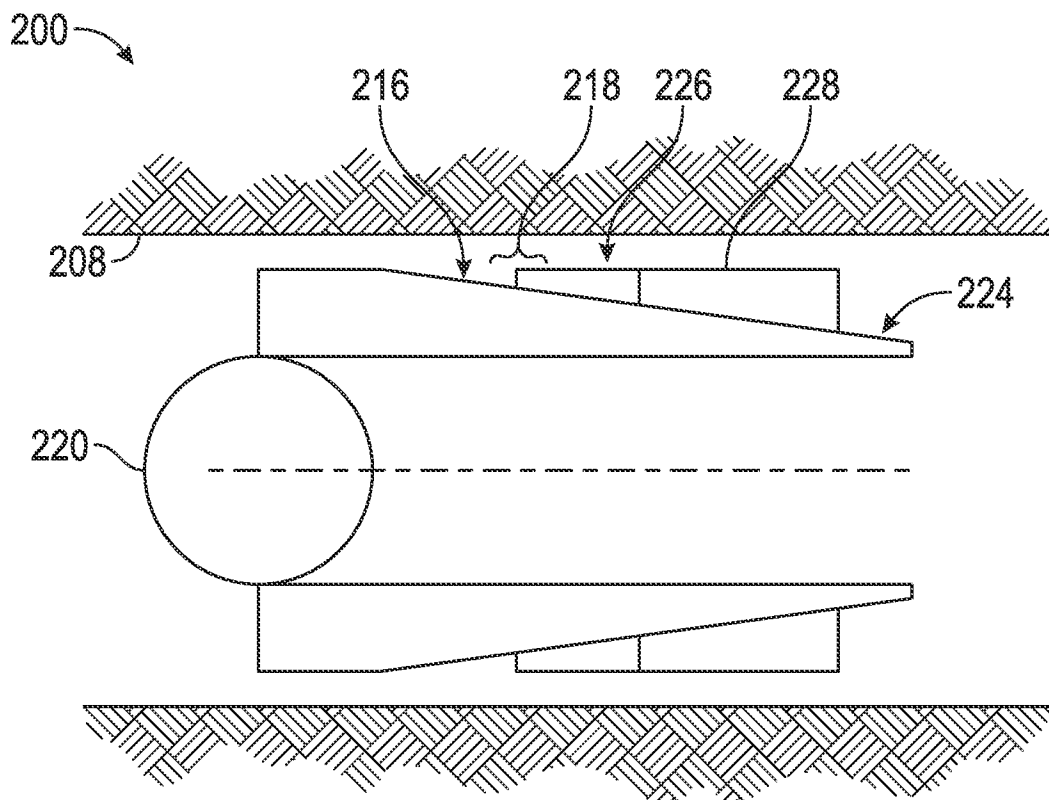


FIG. 2

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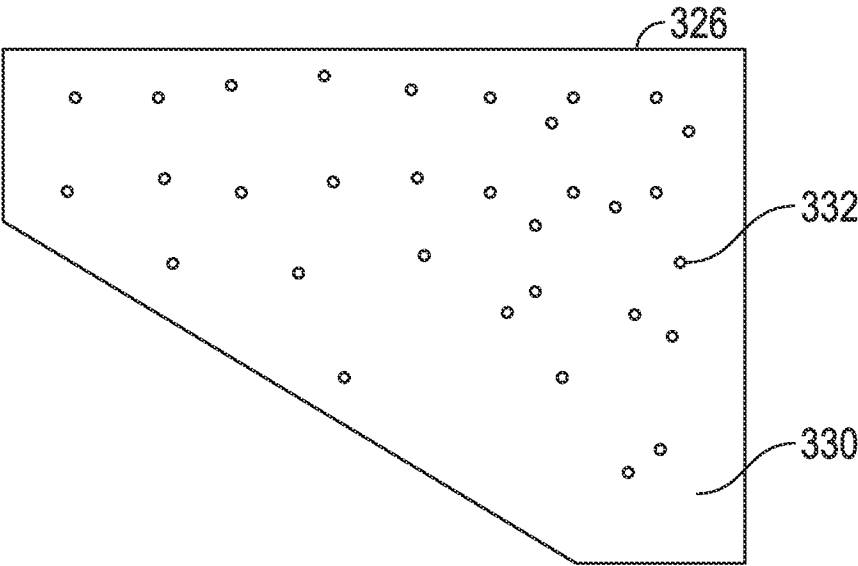


FIG. 3

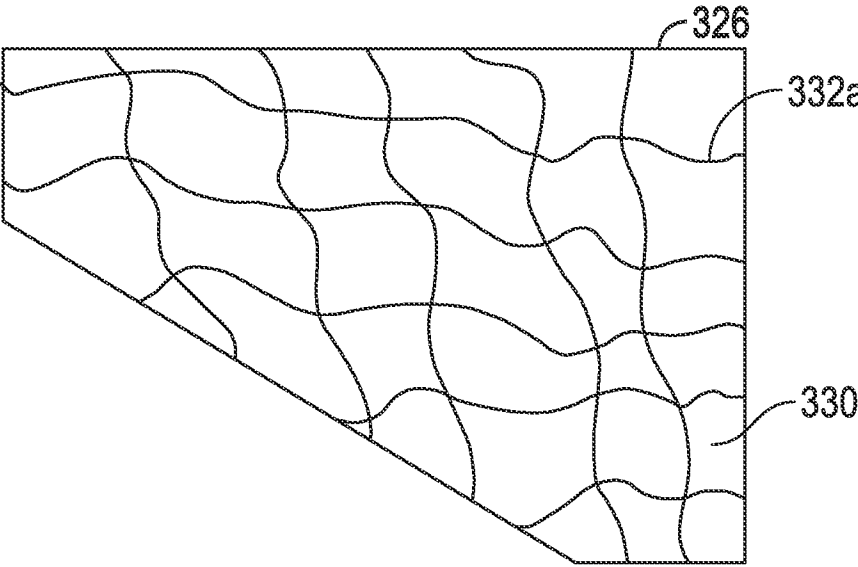


FIG. 3A

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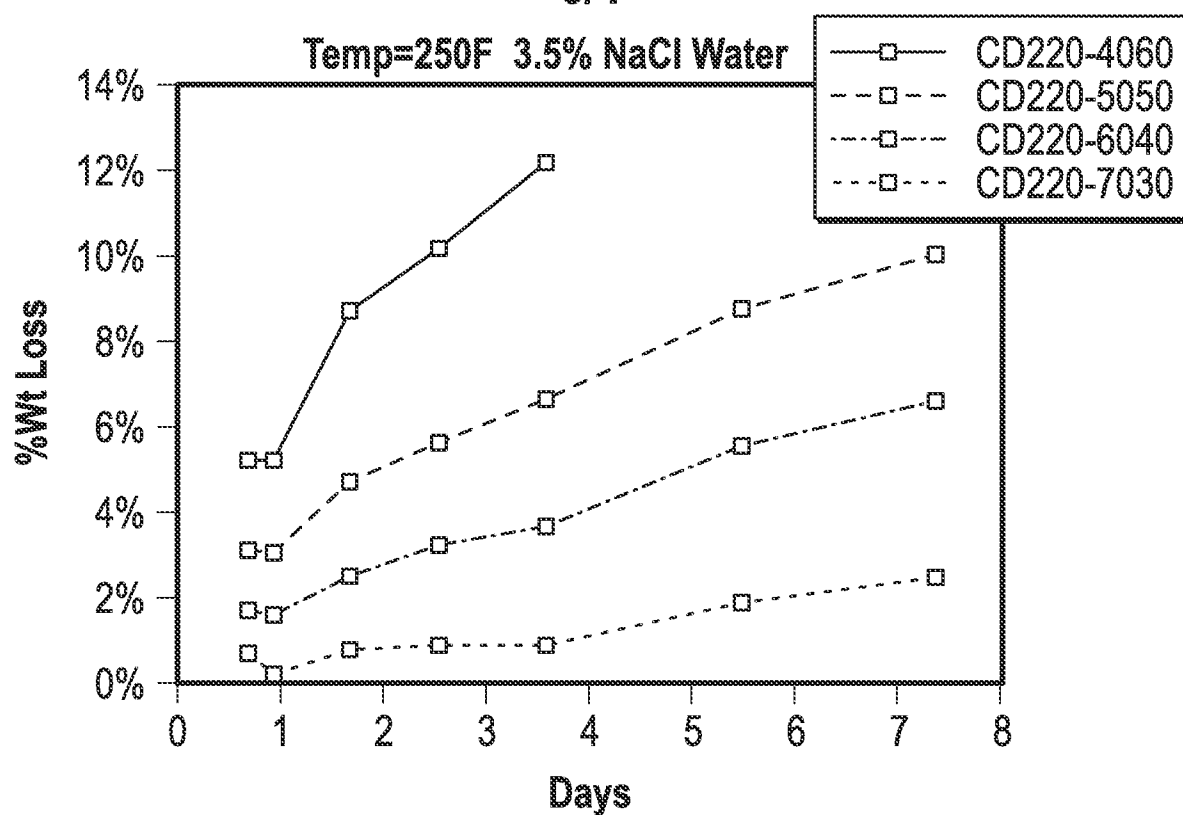


FIG. 4A

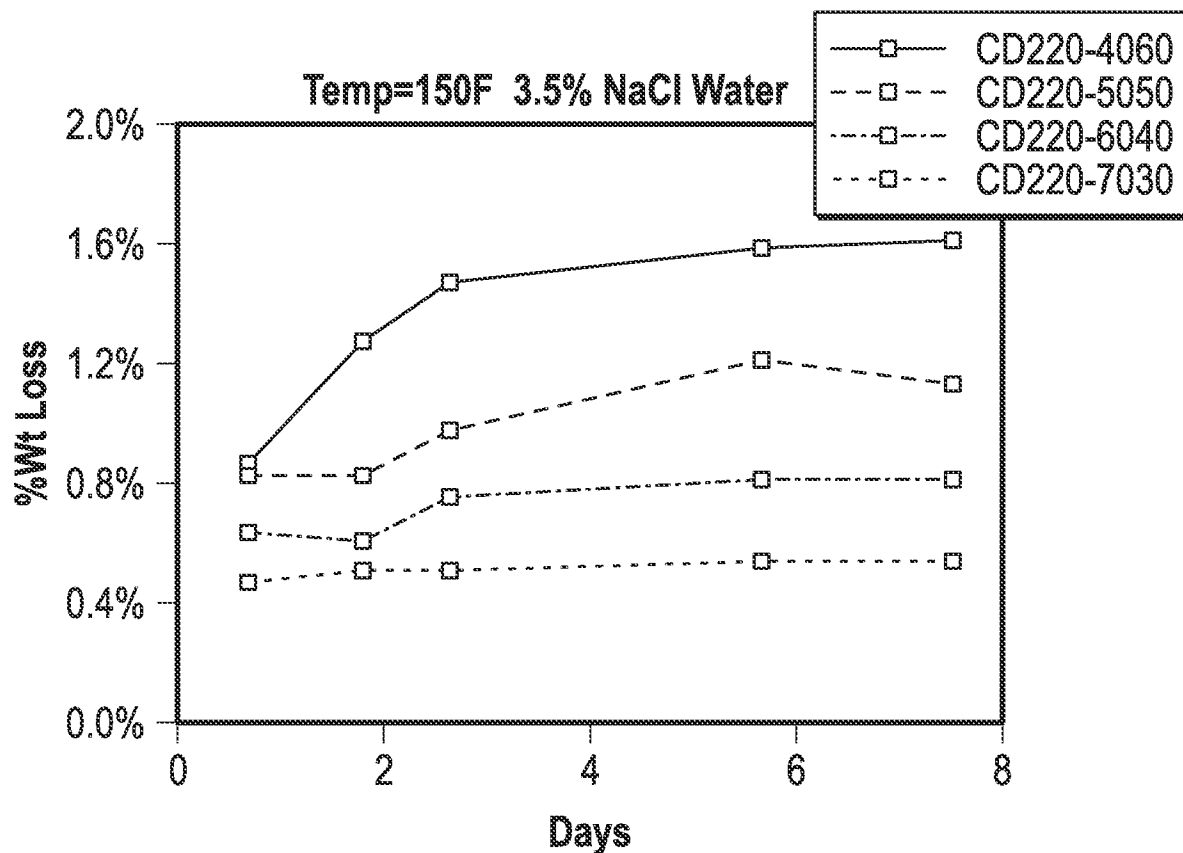


FIG. 4B

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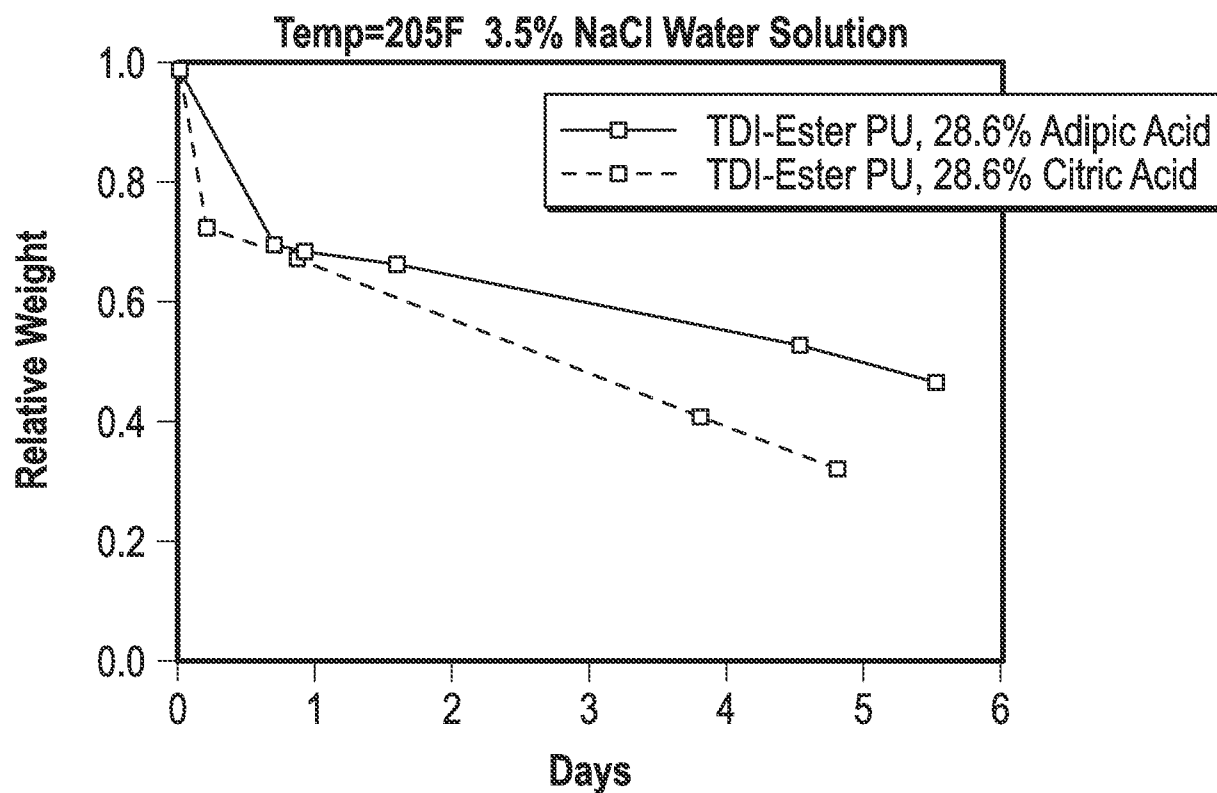


FIG. 4C

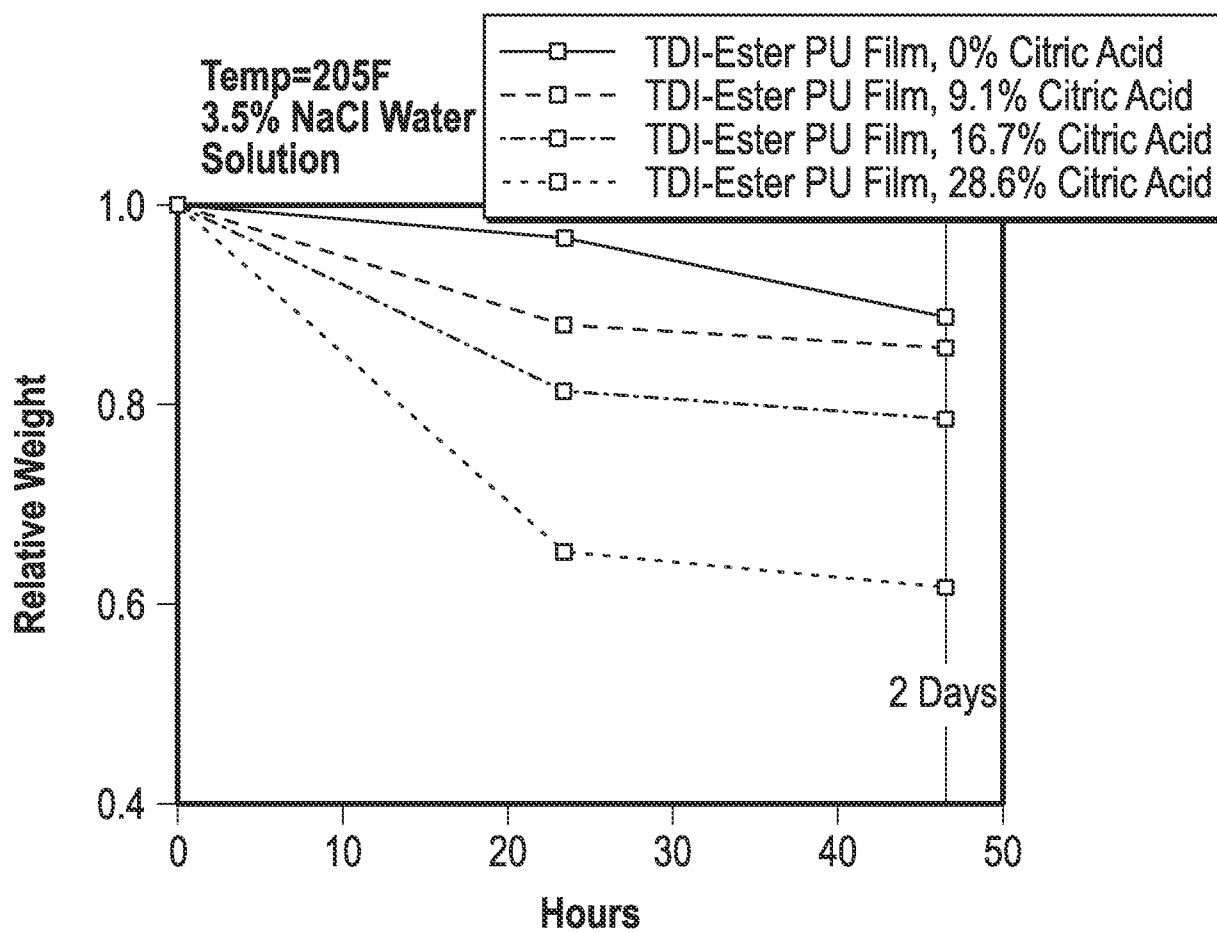


FIG. 4D

## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/US2015/061552****A. CLASSIFICATION OF SUBJECT MATTER****E21B 33/12(2006.01)i, E21B 29/02(2006.01)i, E21B 43/16(2006.01)i, E21B 43/26(2006.01)i**

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)

E21B 33/12; E21B 33/138; C09K 8/72; E21B 33/13; E21B 43/26; C22C 24/00; C22C 21/00; E21B 29/02; E21B 43/16

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) &amp; Keywords:degradable material, polyurethane, corrosive additive, degradation rate, temperature, mix, and casing seal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                               | Relevant to claim No. |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| X         | US 2014-0116701 A1 (HALLIBURTON ENERGY SERVICES, INC.) 01 May 2014<br>See paragraphs [0016], [0039], [0044], [0052], [0065], [0076]–[0077], [0084]–[0086], [0089] and figure 1B. | 1–5                   |
| Y         |                                                                                                                                                                                  | 8–15                  |
| Y         | US 2014-0014339 A1 (O'MALLEY et al.) 16 January 2014<br>See paragraphs [0022]–[0024] and figures 1–2.                                                                            | 8–15                  |
| A         | US 2014-0060834 A1 (BAKER HUGHES INCORPORATED) 06 March 2014<br>See paragraphs [0045]–[0047] and figure 1.                                                                       | 1–5, 8–15             |
| A         | US 2014-0196899 A1 (PARKER-HANNIFIN CORPORATION) 17 July 2014<br>See paragraph [0056] and figure 4.                                                                              | 1–5, 8–15             |
| A         | US 2007-0181224 A1 (MARYA et al.) 09 August 2007<br>See paragraphs [0057]–[0058] and figures 5–6.                                                                                | 1–5, 8–15             |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document 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 when the document is taken alone

"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

"&amp;" document member of the same patent family

Date of the actual completion of the international search

22 February 2016 (22.02.2016)

Date of mailing of the international search report

**23 February 2016 (23.02.2016)**

Name and mailing address of the ISA/KR

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**INTERNATIONAL SEARCH REPORT**International application No.  
**PCT/US2015/061552****Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 6-7  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

**PCT/US2015/061552**

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s)                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   | Publication<br>date                                                                                                                                                                                                                                                                                                                                                                                                                                          |
|-------------------------------------------|---------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
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