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(54) **METHOD AND APPARATUS FOR DELAYED FLOW OR PRESSURE CHANGE IN WELLS**

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**Related U.S. Patent Documents**

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**Y10S 507/925**  
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See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

RE17,217 E 2/1926 Burch  
2,040,889 A 5/1936 Whinnen  
(Continued)

FOREIGN PATENT DOCUMENTS

CA 2891507 6/2014  
EP 2873800 5/2015  
(Continued)

OTHER PUBLICATIONS

Ledlow et al., "Downhole Protection of Sand Control Screens," Society of Petroleum Engineers [SPE], Paper No. 8803, Jan. 1980, 6 pages.

(Continued)

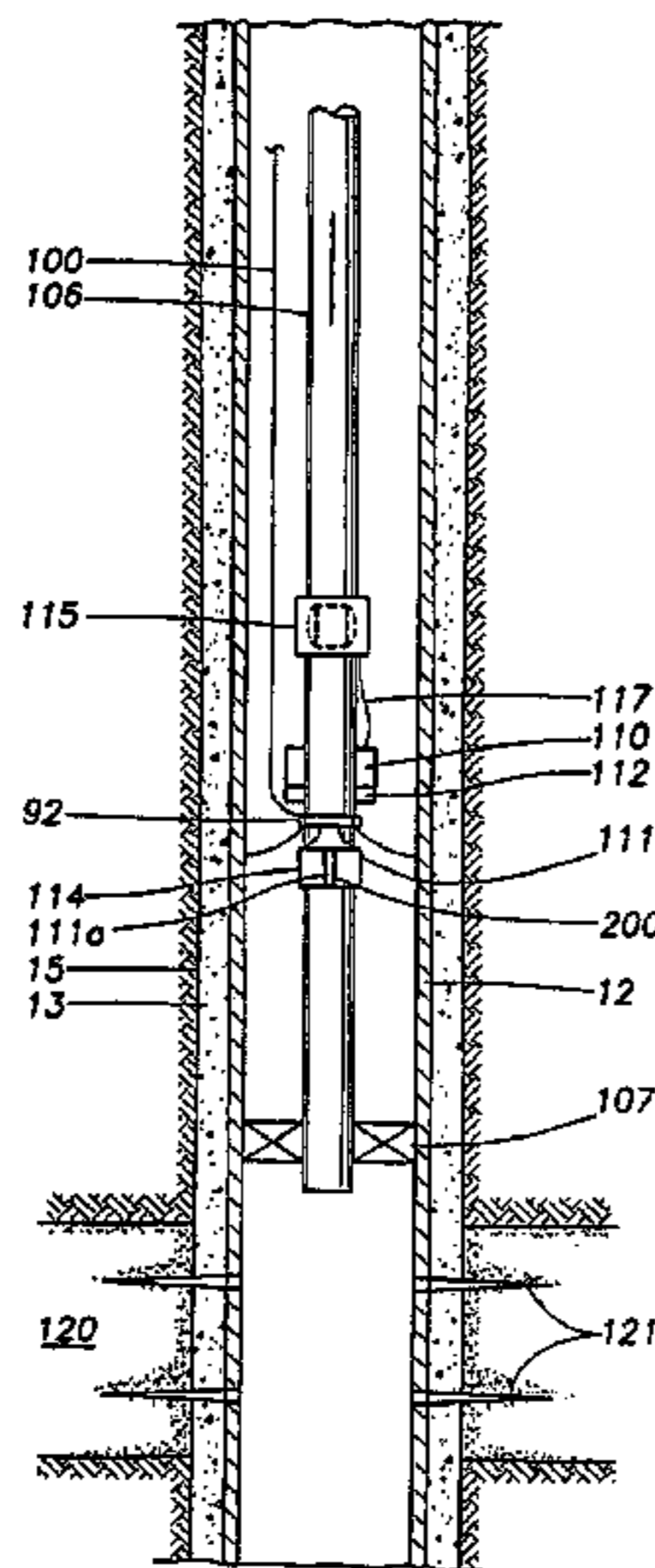
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(57) **ABSTRACT**

Degradable polylactic or polyhydroxyalkanoate polymers may be used to viscosify aqueous fluids for use in wells, Sand control screen or liner can be coated with a solid degradable polymer during placement in a well. Mechanical changes or flow changes in a well can be caused by solid degradable polymer that changes physical properties after it is placed in a well. Parts of devices or entire devices can be made of solid degradable polymer that converts to a fluid after selected times in an aqueous environment in a well.

**7 Claims, 3 Drawing Sheets**



(51)	<b>Int. Cl.</b>		4,405,017 A	9/1983	Allen et al.
	<i>E21B 33/12</i>	(2006.01)	4,432,418 A	2/1984	Mayland
	<i>C09K 8/88</i>	(2006.01)	4,436,151 A	3/1984	Callihan et al.
	<i>C08G 63/08</i>	(2006.01)	4,457,376 A	7/1984	Carmody et al.
	<i>C09K 8/508</i>	(2006.01)	4,502,654 A	3/1985	Albee, Jr.
	<i>C08G 63/06</i>	(2006.01)	4,532,995 A	8/1985	Kaufman
	<i>C09K 8/68</i>	(2006.01)	4,548,442 A	10/1985	Sugden et al.
	<i>C09K 8/512</i>	(2006.01)	4,554,981 A	11/1985	Davies
(52)	<b>U.S. Cl.</b>		4,566,541 A	1/1986	Moussy et al.
	CPC .....	<i>C09K 8/685</i> (2013.01); <i>C09K 8/887</i>	4,585,067 A	4/1986	Blizzard et al.
		(2013.01); <i>C09K 2208/24</i> (2013.01); <i>Y10S</i>	4,595,052 A	6/1986	Kristiansen
		<i>507/903</i> (2013.01); <i>Y10S 507/923</i> (2013.01);	4,688,641 A	8/1987	Knieriemen
		<i>Y10S 507/925</i> (2013.01); <i>Y10S 507/926</i>	4,708,163 A	11/1987	Deaton
		(2013.01)	4,715,967 A	12/1987	Bellis et al.
			D293,798 S	1/1988	Johnson
			4,716,964 A *	1/1988	Erbstoesser et al. .... 166/284
			4,776,410 A	10/1988	Perkin et al.
			4,784,226 A	11/1988	Wyatt
			4,792,000 A	12/1988	Perkin et al.
(56)	<b>References Cited</b>		4,830,103 A	5/1989	Blackwell et al.
	<b>U.S. PATENT DOCUMENTS</b>		4,848,459 A	7/1989	Blackwell et al.
	2,160,228 A	5/1939	4,893,678 A	1/1990	Stokley et al.
	2,223,602 A	12/1940	4,931,490 A	6/1990	Armeniades
	2,230,447 A	2/1941	4,986,353 A	1/1991	Clark et al.
	2,286,126 A	6/1942	4,989,673 A	2/1991	Sydansk
	2,331,532 A	10/1943	5,020,590 A	6/1991	McLeod
	2,555,627 A	6/1951	5,042,598 A	8/1991	Sherman
	2,589,506 A	3/1952	5,052,489 A	10/1991	Carisella et al.
	2,593,520 A	4/1952	5,074,063 A	12/1991	Vannette
	2,616,502 A	11/1952	5,082,061 A	1/1992	Dollison
	2,640,546 A	6/1953	5,095,980 A	3/1992	Watson
	2,713,910 A	7/1955	5,113,940 A	5/1992	Glaser
	2,780,294 A	2/1957	5,115,865 A	5/1992	Carisella et al.
	2,830,666 A	4/1958	5,117,915 A	6/1992	Mueller et al.
	2,833,354 A	5/1958	5,154,428 A	10/1992	Woolhouse
	3,013,612 A	12/1961	5,183,068 A	2/1993	Prosser
	3,054,453 A	9/1962	5,188,182 A	2/1993	Echols, III et al.
	3,062,296 A	11/1962	5,195,583 A	3/1993	Toon et al.
	3,079,997 A	3/1963	5,207,274 A	5/1993	Streich et al.
	3,087,544 A	4/1963	5,209,310 A	5/1993	Clydesdale
	3,088,520 A	5/1963	5,219,380 A	6/1993	Young
	3,126,827 A	3/1964	5,230,390 A	7/1993	Zastresek
	3,141,513 A	7/1964	5,234,052 A	8/1993	Coone
	3,163,225 A	12/1964	5,253,705 A	10/1993	Clary
	3,273,588 A	9/1966	5,295,735 A	3/1994	Cobbs
	3,298,437 A	1/1967	5,316,081 A	5/1994	Baski
	3,298,440 A	1/1967	5,318,131 A	6/1994	Baker
	3,306,362 A	2/1967	D350,887 S	9/1994	Sjolander et al.
	3,308,895 A	3/1967	5,343,954 A	9/1994	Bohlen
	3,356,140 A	12/1967	D353,756 S	12/1994	Graves
	3,362,476 A	1/1968	D355,428 S	2/1995	Hatcher
	3,447,608 A	6/1969	5,390,737 A	2/1995	Jacobi
	3,517,742 A	6/1970	5,392,540 A	2/1995	Cooper
	3,542,130 A *	11/1970	RE35,088 E	11/1995	Gilbert
	3,623,551 A	11/1971	5,476,543 A	12/1995	Ryan
	3,687,202 A	8/1972	5,484,191 A	1/1996	Sollami
	3,818,987 A	6/1974	5,490,339 A	2/1996	Accettola
	3,851,706 A	12/1974	5,509,474 A	4/1996	Cooke, Jr.
	3,860,066 A	1/1975	5,540,279 A	7/1996	Branch
	3,878,101 A	4/1975	5,564,502 A	10/1996	Crow
	3,888,311 A	6/1975	D377,969 S	2/1997	Grantham
	3,926,253 A	12/1975	5,655,614 A	8/1997	Azar
	4,035,024 A	7/1977	5,693,292 A	12/1997	Choperena
	4,049,015 A	9/1977	5,701,959 A	12/1997	Hushbeck
	4,129,308 A	12/1978	5,785,135 A	7/1998	Crawley
	4,134,455 A	1/1979	5,791,825 A	8/1998	Gardner
	4,151,875 A	5/1979	5,803,173 A	9/1998	Fraser
	4,182,423 A	1/1980	5,810,083 A	9/1998	Kilgore
	4,185,689 A	1/1980	5,819,846 A	10/1998	Bolt
	4,189,183 A	2/1980	5,830,991 A	11/1998	Shiiki
	4,191,254 A	3/1980	D415,180 S	10/1999	Rosanwo
	4,222,444 A	9/1980	5,961,185 A	10/1999	Friant
	4,248,299 A	2/1981	5,984,007 A	11/1999	Yuan
	4,250,960 A	2/1981	5,988,277 A	11/1999	Vick
	4,314,608 A	2/1982	5,990,051 A *	11/1999	Ischy et al. .... 507/204
	4,381,038 A	4/1983	6,012,519 A	1/2000	Allen
	4,387,769 A	6/1983	6,082,450 A	7/2000	Snider et al.
	4,391,547 A	7/1983	6,085,446 A	7/2000	Posch
			6,098,716 A	8/2000	Hromas

(56)

References Cited

U.S. PATENT DOCUMENTS

6,105,694 A	8/2000	Scott	D612,875 S	3/2010	Beynon
6,142,226 A	11/2000	Vick	7,673,677 B2	3/2010	King
6,152,232 A	11/2000	Webb	7,681,645 B2	3/2010	McMillin
6,167,963 B1	1/2001	McMahan	D618,715 S	6/2010	Corcoran
6,182,752 B1	2/2001	Smith	7,728,100 B2	6/2010	Sato
6,189,618 B1	2/2001	Beeman	7,735,549 B1	6/2010	Nish
6,199,636 B1	3/2001	Harrison	7,775,286 B2	8/2010	Duphorne
6,220,349 B1	4/2001	Vargus	7,775,291 B2	8/2010	Jacob
6,220,350 B1 *	4/2001	Brothers et al. .... 166/192	7,781,600 B2	8/2010	Ogawa
6,283,148 B1	9/2001	Spears	7,784,550 B2	8/2010	Nutley
6,341,823 B1	1/2002	Sollami	7,798,236 B2	9/2010	McKeachnie
6,367,569 B1	4/2002	Walk	7,810,558 B2	10/2010	Shkurti
6,372,844 B1	4/2002	Shinoda et al	7,812,181 B2	10/2010	Ogawa
6,394,180 B1	5/2002	Berscheidt	D629,820 S	12/2010	Van Ryswyk
6,457,267 B1	10/2002	Porter	7,866,396 B2	1/2011	Rytlewski
6,491,108 B1	12/2002	Slup	7,878,242 B2	2/2011	Gray
6,543,963 B2	4/2003	Bruso	7,886,830 B2	2/2011	Bolding
6,581,681 B1	6/2003	Zimmerman	7,900,696 B1	3/2011	Nish
6,599,863 B1	7/2003	Palmer et al.	7,909,108 B2	3/2011	Swor
6,629,563 B2	10/2003	Doane	7,909,109 B2	3/2011	Angman
6,695,049 B2	2/2004	Ostocke	D635,429 S	4/2011	Hakki
6,725,935 B2	4/2004	Szarka	7,918,278 B2	4/2011	Barbee
6,739,398 B1	5/2004	Yokley	7,921,923 B2	4/2011	McGuire
6,779,948 B2	8/2004	Bruso	7,921,925 B2	4/2011	Maguire
6,799,633 B2	10/2004	McGregor	7,926,571 B2	4/2011	Hofman
6,818,594 B1	11/2004	Freeman et al.	7,926,571 B2	4/2011	Hofman
6,834,717 B2	12/2004	Bland	8,025,104 B2	9/2011	Cooke, Jr.
6,851,489 B2	2/2005	Hinds	8,039,548 B2	10/2011	Ogawa et al.
6,852,827 B2	2/2005	Yamane	8,074,718 B2	12/2011	Roberts
6,854,201 B1	2/2005	Hunter	8,113,276 B2	2/2012	Greenlee et al.
6,868,911 B1	3/2005	Jacobson et al.	8,127,856 B1	3/2012	Nish et al.
6,891,048 B2	5/2005	Yamane	D657,807 S	4/2012	Frazier
6,902,006 B2	6/2005	Myerley	8,231,947 B2	7/2012	Vaidya et al.
6,916,939 B2	7/2005	Yamane	8,304,500 B2	11/2012	Sato et al.
6,918,439 B2	7/2005	Dallas	8,318,837 B2	11/2012	Sato et al.
6,938,696 B2	9/2005	Dallas	8,362,158 B2	1/2013	Sato et al.
6,944,977 B2	9/2005	Deniau	8,404,868 B2	3/2013	Yamane et al.
6,949,491 B2	9/2005	Cooke, Jr.	8,580,914 B2	11/2013	Sato et al.
7,040,410 B2	5/2006	McGuire	8,658,758 B2	2/2014	Sato et al.
7,055,632 B2	6/2006	Dallas	8,691,912 B2	4/2014	Suzuki et al.
7,059,410 B2	6/2006	Bousche et al.	8,722,907 B2	5/2014	Suzuki et al.
7,067,611 B2	6/2006	Yamane	8,722,908 B2	5/2014	Suzuki et al.
7,069,997 B2	7/2006	Coyes	2001/0040035 A1	11/2001	Appleton et al.
7,093,664 B2	8/2006	Todd	2002/0142919 A1	10/2002	Constein
7,107,875 B2	9/2006	Haugen	2003/0024706 A1	2/2003	Allamon
7,124,831 B2	10/2006	Turley	2003/0060374 A1	3/2003	Cooke, Jr.
7,128,091 B2	10/2006	Istre	2003/0188860 A1	10/2003	Krueger
7,134,505 B2	11/2006	Fehr	2004/0015033 A1	1/2004	Steiner
7,150,131 B2	12/2006	Barker	2004/0094300 A1	5/2004	Sullivan et al.
7,168,494 B2	1/2007	Starr	2004/0106525 A1	6/2004	Willberg et al.
7,196,040 B2	3/2007	Heath et al.	2004/0114463 A1	6/2004	Berg et al.
7,235,673 B2	6/2007	Yamane	2004/0149431 A1	8/2004	Wylie et al.
7,281,584 B2	10/2007	McGarian	2004/0216876 A1	11/2004	Lee
D560,109 S	1/2008	Huang	2004/0231845 A1	11/2004	Cooke, Jr.
7,325,617 B2	2/2008	Murray	2005/0065037 A1 *	3/2005	Constien ..... 507/203
7,337,847 B2	3/2008	McGarian	2005/0130845 A1 *	6/2005	Freeman et al. .... 507/100
7,353,879 B2	4/2008	Todd et al.	2005/0173126 A1	8/2005	Starr et al.
7,363,967 B2	4/2008	Burriss	2005/0205266 A1	9/2005	Todd et al.
7,373,973 B2	5/2008	Smith	2005/0233425 A1	10/2005	Matsumura
D579,110 S	10/2008	Zink, II et al.	2005/0241825 A1	11/2005	Burriss et al.
7,464,764 B2	12/2008	Xu	2005/0241827 A1	11/2005	Whitfill et al.
7,501,464 B2	3/2009	Sato	2006/0001283 A1	1/2006	Larsen
7,527,104 B2	5/2009	Branch	2006/0011389 A1	1/2006	Locati
7,538,178 B2	5/2009	Sato	2006/0229212 A1	10/2006	Willberg et al.
7,538,179 B2	5/2009	Sato	2006/0278405 A1	12/2006	Turley et al.
7,552,779 B2	6/2009	Murray	2007/0051521 A1	3/2007	Fike et al.
7,600,572 B2	10/2009	Slup	2007/0068670 A1	3/2007	Booth
7,604,058 B2	10/2009	McGuire	2007/0107908 A1	5/2007	Vaidya et al.
7,622,546 B2	11/2009	Sato	2007/0225175 A1	9/2007	Cooke, Jr.
7,625,846 B2	12/2009	Cooke	2007/0227745 A1	10/2007	Roberts et al.
7,637,326 B2	12/2009	Bolding	2007/0240883 A1	10/2007	Telfer
7,644,767 B2	1/2010	Kalb	2008/0015120 A1	1/2008	Cooke, Jr.
7,644,772 B2	1/2010	Avant	2008/0110635 A1	5/2008	Loretz et al.
7,644,774 B2	1/2010	Branch	2008/0115932 A1	5/2008	Cooke, Jr.
7,647,964 B2	1/2010	Akbar	2009/0044957 A1	2/2009	Cho
			2009/0107684 A1	4/2009	Cooke, Jr.
			2009/0114401 A1	5/2009	Purkis
			2009/0126933 A1	5/2009	Telfer
			2009/0211749 A1	8/2009	Nguyen et al.
			2010/0064859 A1	3/2010	Stephens

(56)

## References Cited

## U.S. PATENT DOCUMENTS

2010/0084146 A1 4/2010 Roberts  
 2010/0101803 A1 4/2010 Clayton et al.  
 2010/0132960 A1 6/2010 Shkurti et al.  
 2010/0155050 A1 6/2010 Frazier  
 2010/0252252 A1 10/2010 Harris et al.  
 2010/0276159 A1 11/2010 Mailand et al.  
 2010/0288503 A1 11/2010 Cuiper et al.  
 2011/0005779 A1 1/2011 Lembcke  
 2011/0036564 A1 2/2011 Williamson  
 2011/0061856 A1 3/2011 Kellner et al.  
 2011/0088915 A1 4/2011 Stanojcic et al.  
 2011/0103915 A1 5/2011 Tedeschi  
 2011/0168404 A1 7/2011 Telfer et al.  
 2011/0198082 A1 8/2011 Stromquist et al.  
 2011/0240295 A1 10/2011 Porter et al.  
 2011/0259610 A1 10/2011 Shkurti et al.  
 2012/0181032 A1 7/2012 Naedler et al.  
 2013/0008666 A1 1/2013 Cherewyk  
 2013/0008671 A1 1/2013 Booth  
 2013/0014936 A1 1/2013 Griffith  
 2013/0068474 A1 3/2013 Hofman et al.  
 2013/0292123 A1 11/2013 Murphree et al.  
 2013/0300066 A1 11/2013 Xu  
 2013/0306327 A1 11/2013 Williamson  
 2013/0319668 A1 12/2013 Tschetter  
 2013/0319682 A1 12/2013 Tschetter  
 2013/0333891 A1 12/2013 Fripp  
 2014/0000894 A1 1/2014 Coffey  
 2014/0020911 A1 1/2014 Martinez  
 2014/0027127 A1 1/2014 Frazier et al.  
 2014/0027128 A1 1/2014 Johnson  
 2014/0041857 A1 2/2014 Xu  
 2014/0060813 A1 3/2014 Naedler  
 2014/0076571 A1 3/2014 Frazier et al.  
 2014/0083717 A1 3/2014 Frazier et al.  
 2014/0096970 A1 4/2014 Andrew  
 2014/0102709 A1 4/2014 Arabskyy  
 2014/0110112 A1 4/2014 Jordan, Jr.  
 2014/0116677 A1 5/2014 Sherlin  
 2014/0116721 A1 5/2014 Hofman  
 2014/0116731 A1 5/2014 Themig  
 2014/0116775 A1 5/2014 Coffey  
 2014/0182862 A1 7/2014 Derby  
 2014/0190685 A1 7/2014 Frazier et al.  
 2014/0196899 A1 7/2014 Jordan  
 2014/0224476 A1 8/2014 Frazier  
 2014/0224477 A1 8/2014 Wiese  
 2014/0231069 A1 8/2014 VanLue  
 2014/0231099 A1 8/2014 Barbee

2014/0246189 A1 9/2014 Beason  
 2014/0246208 A1 9/2014 Themig  
 2014/0248448 A1 9/2014 Sjostedt  
 2014/0251594 A1 9/2014 Garcia  
 2014/0251612 A1 9/2014 Powers  
 2014/0251636 A1 9/2014 Hofman  
 2015/0090440 A1 4/2015 Cooke  
 2015/0144348 A1 5/2015 Okura et al.

## FOREIGN PATENT DOCUMENTS

GB 914030 12/1962  
 JP 2001-178483 7/2001  
 RU 2057780 C1 4/1996  
 SU 505794 3/1976  
 SU 1501597 10/1991  
 SU 1723309 3/1992  
 WO WO2001094744 12/2001  
 WO WO2010127457 11/2010  
 WO WO2014010267 1/2014  
 WO WO2014024827 2/2014  
 WO WO2014077302 5/2014  
 WO WO2014092067 6/2014  
 WO WO2014109347 7/2014  
 WO WO2014192885 12/2014  
 WO WO2014208527 12/2014  
 WO WO2015060246 4/2015  
 WO WO2015060247 4/2015  
 WO WO2015098597 7/2015  
 WO WO2015098801 7/2015  
 WO WO2015098803 7/2015  
 WO WO2015098849 7/2015  
 WO WO 2015098913 7/2015  
 WO WO 2015099005 7/2015

## OTHER PUBLICATIONS

Li et al., "Further investigations on the hydrolytic degradation of poly (DL-lactide)," *Biomaterials*, 20(1):35-44, Jan. 1999.  
 Penner, "The durability of selected geotextile fabrics to heavy oil well fluids," University of Alberta [thesis], Oct. 1990, 104 pages.  
 Sodergard et al., "Properties of lactic acid based polymers and their correlation with composition," *Prog Polym Sci.*, 27 (6):1123-1163, Jul. 2002.  
 Vert et al., "Present and future of PLA polymers," *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, A32(4):787-796, Apr. 1, 1995.  
 Weiler et al., "Enhancement of the mechanical properties of polylactides by solid-state extrusion. I. Poly(D-lactide)," *Biomaterials*, 17(5):529-535, Mar. 1996.

\* cited by examiner

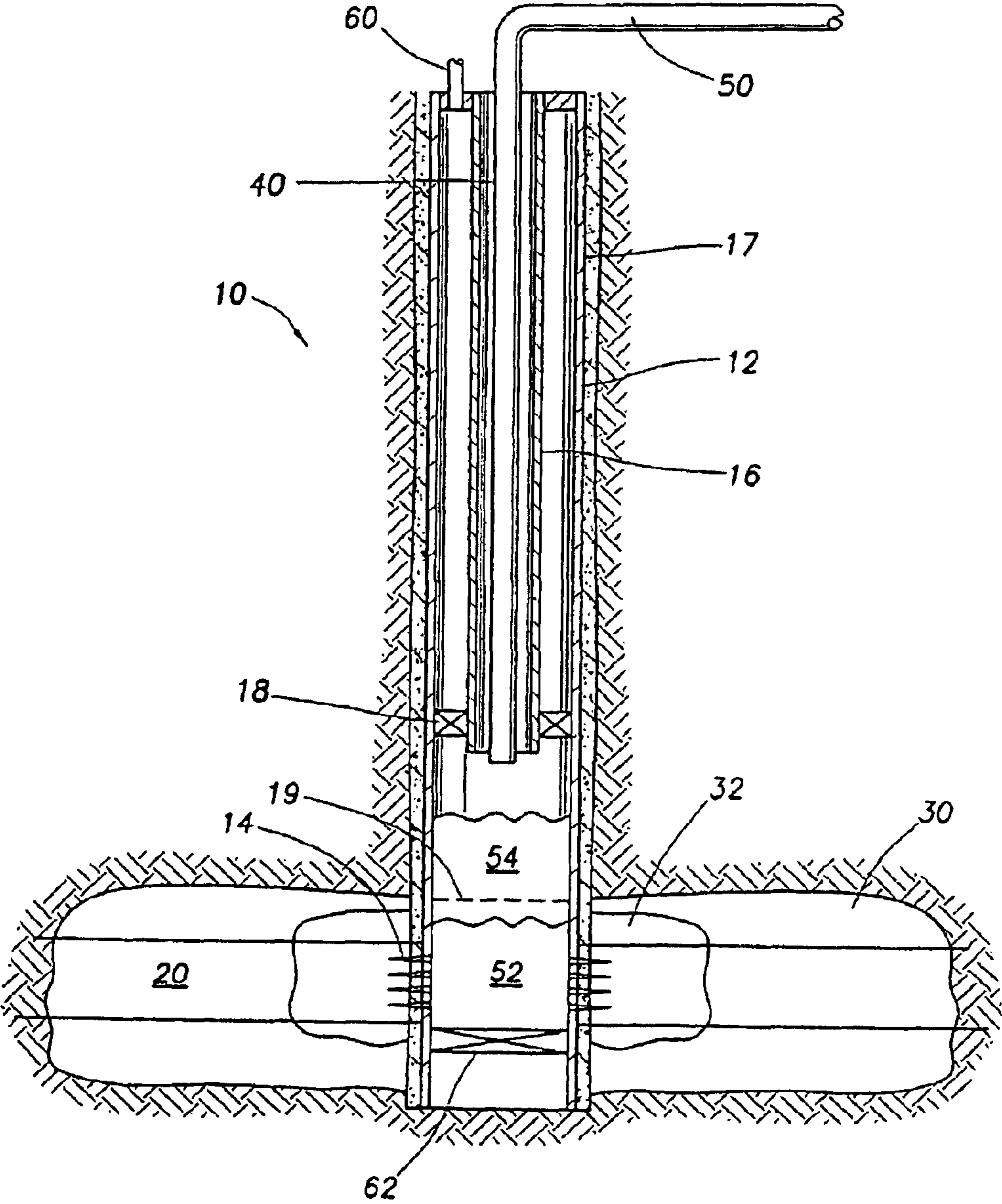


FIG. 1

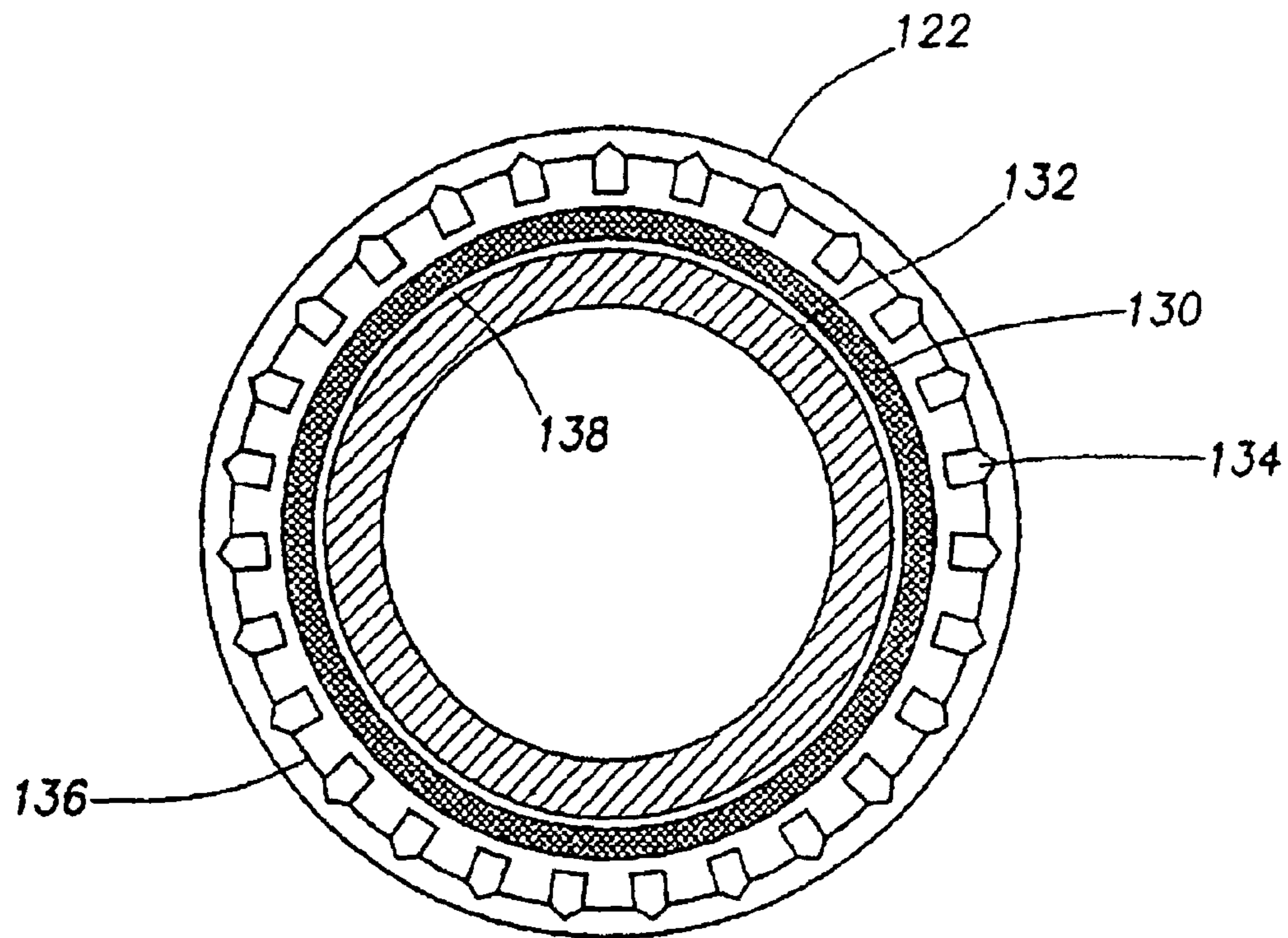


FIG.2

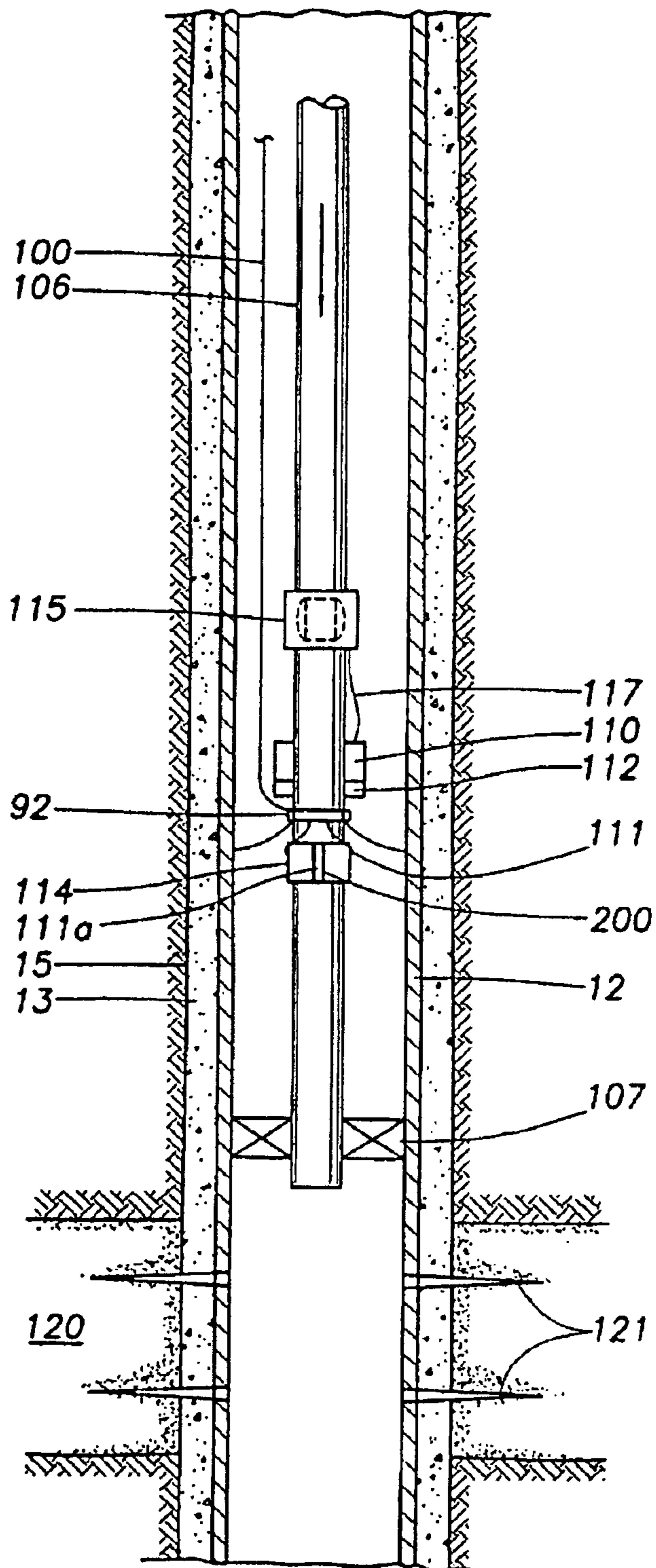


FIG.3

## METHOD AND APPARATUS FOR DELAYED FLOW OR PRESSURE CHANGE IN WELLS

**Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue; a claim printed with strikethrough indicates that the claim was canceled, disclaimed, or held invalid by a prior post-patent action or proceeding.**

This application is a divisional application of application Ser. No. 11/804,612 filed May 18, 2007, now U.S. Pat. No. 7,625,846, which is a continuation of U.S. application Ser. No. 10/845,737, filed May 14, 2004, now abandoned, which claims the benefit of U.S. Provisional Application No. 60/470,738, filed May 15, 2003.

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

This invention pertains to mechanical and chemical operations in wells. In one embodiment, polymer and method of preparing viscous fluid for use in wells is provided. In another embodiment, material and methods are provided for coating of sand control screens used in wellbores. In another embodiment, this invention pertains to delayed mechanical or flow changes in a wellbore after equipment is placed in the well. In another embodiment, this invention pertains to equipment that is placed in a wellbore and is degraded in the wellbore by contact with aqueous fluid.

#### 2. Discussion of Related Art

A large number of mechanical and chemical operations are carried out in and around wells. Most of these wells are used for producing hydrocarbons from the earth. They are located at depths ranging from a few hundred feet below the surface of the earth to more than 30,000 feet. The temperature at the bottom of the wells likewise varies over a wide range—from about 100° F. to more than 400° F.

After the hole is drilled in the earth in the process of constructing a well, the process of placing casing in the well and cementing it in place is commenced. Mechanical devices to aid in the cementing process may be placed on the outside of the casing before it is placed in the hole. Instruments and communication cables may be placed on the casing. Multiple lateral holes may be drilled from a single hole and casing may be placed in each. When casing has been cemented, the process of “completing” the well may begin. This involves forming holes (“perforating”) the casing opposite an interval of a formation where fluids are to be produced or injected and, in most cases, placing tubing in the well. Various types of mechanical equipment may be placed in the wellbore, for safety, flow control and other purposes. Viscous, non-damaging fluids having a selected specific gravity are needed in wells during completion operations. In many wells various types of treatment fluids are then injected into the well to provide greater capacity of the well to produce hydrocarbons, in processes such as hydraulic fracturing and acidizing, called “stimulation” processes. The use of a degradable polymer in the form of ball sealers or particulates to divert fluid or control fluid loss from a well during completion or stimulation operations has been disclosed. (U.S. Pat. No. 4,716,964)

In some wells, the formation where hydrocarbons are found has low mechanical strength, which can result in “sand” being produced into the well along with hydrocarbons. The well then requires application of a “sand control”

process. One of these processes requires placing a “screen” in the well. The solid particles (cuttings) and drilling fluid in the well may plug or partially plug the screen as it is placed in a well. This problem can be particularly severe in directional or horizontal wells. A recent U.S. Patent Application Publication (US2002/0142919 A1) discloses screen coatings that melt or dissolve within a wellbore and release reactive materials effective in degrading or dissolving materials that could plug a screen. The problem of screen plugging during placement was recognized many years ago (“Downhole Protection of Sand Control Screens,” Society of Petroleum Engineers Paper No. 8803, 1980).

In well operations used for completing or stimulating a well, viscous fluids may be used. In most cases, it is desirable that the fluid become lower viscosity with time after it is placed in a well or formation around a well. When the fluid becomes low viscosity it should contain no significant amount of solid or gel material. One example application of such fluids is hydraulic fracturing of wells. U.S. Patent Application Publication 2003/0060374A1, which is hereby incorporated by reference herein, discloses the use of highly concentrated degradable polymers in an aqueous liquid in such application. As explained in that Publication, there is a need for fracturing fluids that degrade to low viscosity without leaving a residue.

Other applications where a viscous fluid may be injected into a well or used in a well include completion fluids, perforating fluids and fluids for carrying gravel (sand) into a well. These fluids are preferably solids-free and degradable to low viscosity fluid having low solid or gel content that could degrade permeability of a porous rock. Other applications where a viscous liquid in a wellbore may be advantageous include a completion or workover fluid that is placed in a well during running of a mechanical device into the well or other mechanical operation in the well. These fluids may contain high concentrations of compounds soluble in water that increase the density of the fluid, such as sodium bromide or zinc bromide, or solid weighting materials. The viscosifying material in the fluids should degrade with time and leave little or no residue of solid or gel that could damage the permeability of a formation around the well.

A wide variety of mechanical devices are placed in wells during completion and workover operations. These devices are used to control fluid flow, to seal around tubulars in the well, to perform measurements of physical or chemical parameters and various other purposes. These devices may be needed for only a limited time and then an operator may wish to have them no longer effective or to no longer have mechanical strength. For example, packers, bridge plugs and cement retainers may be needed for a limited time in a well. There may be a need to release a mechanical device or open a port after a selected time in an inaccessible portion of a wellbore, such as in an annulus between tubular strings, where an aqueous fluid is located.

What are needed in a variety of well operations or processes are viscous liquids that degrade to low viscosity liquid at a predictable rate and leave low amounts of solid or gel residue, a degradable coating for screens, and solids that lose mechanical strength at a predictable rate in the presence of an aqueous liquid to allow delayed flow or mechanical changes in inaccessible locations in wellbores or degradation of mechanical equipment that is no longer needed in a wellbore.

### SUMMARY OF THE INVENTION

Degradable polymers and methods for using in wells are provided. In one embodiment, the degradable polymer is used



to viscosify fluids used in wellbore operations. In another embodiment, the degradable polymer is used to protect a sand control screen from plugging as it is placed in a well. In yet another embodiment, the degradable polymer is used to delay to a selected range of time a change in mechanical or flow conditions in a well. In yet another embodiment, the solid degradable polymer is used to form equipment that is temporarily used in well operations.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a sketch of a cased well having tubing and the surrounding formation.

FIG. 2 shows a cross-section of a wire-wrapped sand control screen protected by a degradable polymer.

FIG. 3 shows spring-loaded apparatus in the annulus between tubing and casing in a well that is released by degradation of a degradable polymer.

#### DETAILED DESCRIPTION OF THE INVENTION

Referring to FIG. 1, wellbore **10** penetrates formation **20** where fluid is to be produced or injected. Wellbore **10** has casing **12** extending through formation **20**, casing **12** being cemented in place by cement sheath **17**. Perforations **14** have been formed through the wall of casing **12** and cement sheath **17** into formation **20**. Perforations **14** may extend over the entire thickness of formation **20** or may extend only over a selected interval of formation **20** less than the total thickness surrounding wellbore **10**. In some wells, hydraulic fracture **30** may have been formed around wellbore **10** by a previous treatment employing conventional fracturing fluid and proppant, using techniques well-known in industry. Alternatively, fracture **30** may not be present. Tubing **16** may have been suspended inside casing **12** and packer **18** may have been set near the bottom of tubing **16** to seal the annulus between tubing **16** and casing **12**. Packer **18** may not be present in some wells, tubing **16** may not be present in some wells, and even casing **12** may not be present in some wells, although most wells in which the methods disclosed here will be applied contain casing and tubing with a packer near the bottom of the tubing. Packer **18** may have a controllable port for circulating fluids in the annulus of the well (not shown) or tubing **16** may be releasable from packer **18** to allow circulation of fluids down the tubing and up the tubing-casing annulus. Alternatively, tubing **16** may contain a sliding sleeve above and near packer **18**, which is well known in industry.

In an embodiment for damage removal near wellbore **10**, the materials and methods disclosed in U.S. Patent Application Publication 2003/0060374A1, which is incorporated by reference, may be used to form short hydraulic fracture **32** around wellbore **10** by injecting the degradable fracturing fluid at a pressure above the fracturing pressure of formation **20**. The fracturing fluid disclosed herein is similar to fracturing fluids normally used, in which a polymer is dispersed in a liquid to increase viscosity of the liquid, and has rheological properties similar to the conventional fracturing fluids. The fracturing fluid disclosed herein is a more dilute mixture of the degradable polymer contained in the "polymer phase" disclosed in the cited '374 Publication, and it may be used to form hydraulic fracture **30** or hydraulic fracture **32**, as shown in FIG. 1. The preferred degradable polymer is a polymer that is polymerized to a preferred range of molecular weight or is degraded (decreased in molecular weight) by reaction with water (herein "water-degradable") to a desirable range of molecular weight for use in a wellbore fluid. The polymer is dispersed or dissolved in an aqueous liquid and then degrades

to mostly water-soluble monomers or oligomers over a period of time in the presence of water.

The use of solid water-degradable polymers in wells is known. Their use in wellbores for diverting fluids between perforations or decreasing fluid loss from a hydraulic fracture when particles of the polymer are dispersed in fracturing fluid has been disclosed. U.S. Pat. No. 4,716,964 discloses use of such polymers in "ball sealers" and as a fluid loss material in well treating fluids. Ball sealers are rigid spheres added to a well treatment fluid to seal on perforations and divert flow of the treatment fluid to other perforations. Fluid loss additives are finely divided solid polymer particles that are dispersed in the fracturing fluid or other well treatment fluid and injected into a well. The polymers disclosed in the '964 patent include poly (D,L-lactide) and copolymers of lactide and glycolide.

A significant amount of research and development has been performed in recent years to commercialize polymers that degrade to water-soluble chemicals. In addition to the polylactic acid (PLA) polymers commercialized by Cargill Dow Polymers LLC, other degradable polymers, including other polyesters (based on polyethylene terephthalate, for example), starches, polycaprolactone, polyhydroxybutyrates and blends of these materials have been developed. Properties of lactide polymers are reviewed in the article "Properties of lactic acid based polymers and their correlation with composition," A. Sodergard and M. Stolt, Prog. in Pol. Sci., July, 2002. Further development is underway for other degradable or biodegradable polymers. Metabolix, Inc. of Cambridge, Mass., for example, is developing a family of degradable polymers known as PHAs (polyhydroxyalkanoates). PHA polymers (also polyesters) are produced by photosynthesis, either indirectly using highly efficient fermentation processes, or directly in plant crops. The price of these polymers is expected to decrease to about the cost of oil-derived polymers within a few years. The properties of such polymers can be adjusted by molecular weight distribution, crystallinity, co-polymers and additives to control physical properties and degradation time under selected environments. Polymers such as PLAs and selected PHAs, such as polyhydroxybutyrate, can be optimized for the applications disclosed herein by varying manufacturing methods and conditions. Polyhydroxybutyrate will be, in general, more stable to degradation than PLA. Different polymerization variables can be controlled during manufacture and/or compounding to provide desirable degradation times under a broad range of environmental conditions that exist in underground formations. The PHAs can also be optimized by varying microbes used in the fermentation processes.

Degradation of solid polyesters occurs first by water penetrating the bulk of the polymer, preferentially attacking the chemical bonds in the amorphous polymer and converting long chains into shorter water-soluble fragments. Degradation rates can be controlled by incorporation of various additives. The control of properties of thermoplastic polymers by addition of plasticizers and other additives is well known. Of course, exposure of the plastics to moisture before their use can be controlled to prevent premature degradation. Biodegradable polymers may also be degraded by enzymes, which may be used to contact the polymers, as is known in the art. If there is need to increase the degradation rate of polymers left in a wellbore, for example, heating of the polymers in the wellbore can be used to increase degradation rate or the polymer may be contacted by a solution containing enzymes. The Sodergard and Stolt article, cited above, discusses biodegradation of degradable polymers, including polyesters, and polylactic acid in particular. The degradation rate (hy-

drolysis) of polylactic acids may be increased significantly by enzymes pronase, proteinase K and bromelain.

Since water is always present in hydrocarbon reservoirs and aqueous liquids are usually used in wellbore operations, there is nearly always a mechanism to cause polymer degradation of water-degradable polymers in a wellbore or in a reservoir. Rate of polymer degradation will depend primarily on polymer composition, polymer structure and temperature. For any degradable polymer selected, degradation time can be determined by heating a sample of the polymer to be injected. A water-degradable polymer can be exposed to an aqueous liquid and subjected to a thermal history simulating the conditions the polymer would experience in a well where it is to be used. The thermal history of the polymer as it is placed in a wellbore or injected down a wellbore and resides in the wellbore or the subsurface formation while degrading may be simulated in laboratory tests to select the polymer or copolymers and any additives used with the polymer.

A fracturing fluid, completion or workover wellbore fluid, fluid for carrying gravel into a fracpack or gravel pack or fluid for other well operations may be formed by polymerizing lactic acid to PLA or forming PHA or other biopolymer having a range of molecular weight that can be dissolved in an aqueous liquid to be used in the well operation and adding the resulting polymer to aqueous liquid. If the molecular weight of the manufactured PLA or PHA is too high to allow solubility in the aqueous liquid, the molecular weight of the polymer can be decreased by applying heat to the polymer in the presence of water. For example, steam or hot water may be applied to solid or liquid polymer for a selected time to obtain a molecular weight range of the polymer such that it can be dissolved in the aqueous liquid to be used in a well operation. Polymer having a desired range of molecular weight may be stabilized or partially stabilized against further decrease of molecular weight until it is used in a well operation by removing water from the polymer (drying) or by lowering the temperature of the polymer in an aqueous fluid.

The well treatment fluid disclosed herein may be placed in wellbore 10 (FIG. 1) by pumping the viscous polymer down the well from the surface as fluids of the prior art are pumped. The polymer is added to the aqueous well treatment fluid to a concentration selected to achieve the desired range of viscosity of the treatment fluid. The polymer may be cross-linked to increase the effective viscosity of the solution using well known cross-linking agents.

The properties of polylactide are affected by the isomeric content of the polymer. In addition to the D, L-polylactide disclosed in U.S. Pat. No. 4,716,964, discussed above, which is a racemic mixture, a polylactide formed from 13 percent D-isomer and 87 percent L-isomer, available from Cargill-Dow, is primarily amorphous in the solid state and degrades to form a viscous liquid in the presence of water. Preferably, a polymer that is amorphous or not highly crystalline in the solid state will be used to form the well treatment fluid of this invention. At the boiling point of water, viscous liquid formed from solid pellets of the 13 percent D-isomer material, whereas a polylactide containing only about 6 percent D-isomer did not degrade to a viscous liquid under the same conditions but degraded to a crystalline polymer. Therefore, the relative amount of D- and L-isomer should be selected in the range from about 10 percent to about 90 percent of an isomer or in a range to form an amorphous or not highly crystalline polymer. It is believed that isomer compositions in this range form an amorphous polymer and the lower molecular weight polymers and the oligomers formed during degradation form less crystalline material, allowing formation of the viscous liquid during degradation of the polymer. The viscous liquid

can be diluted to form a solution having desired rheological properties. Amorphous forms of other polyesters are preferred for the same reasons.

In addition to the application of degradable polymers to form viscous aqueous liquid for use in wells, the polymers may be applied in the solid form in a variety of processes or methods. The primary characteristic of the polymer in some of these applications is that the mechanical properties of the polymer change in a predictable manner with time in the presence of water or an aqueous liquid. If desired, an initial solid polymer may finally go in solution in the aqueous phase. In some applications, only a decrease in mechanical properties (modulus, bending strength, tensile or compressive strength, for example) in a predictable time range may be necessary for application of the polymer. In other applications, the polymer may maintain its mechanical properties until it is employed, then decrease in mechanical properties and become a low-strength gel or low-strength crystalline solid or become soluble in an aqueous phase in a wellbore.

In one embodiment of the invention disclosed herein, degradable polymer is used to coat a sand control screen or slotted liner before it is placed in a well. Such an application is described in a recently published U.S. Patent Application (No. 2002/0142919A1), which is hereby incorporated by reference. The material used to coat the screen is called a "binder." In the '919 Publication, it is disclosed that the binder may contain components that "react with potentially plugging materials in the near wellbore area" when the components are released as the binder melts or dissolves. Such components are well known (scale, paraffin and clays, for example). The use of wax and soluble solids as a binder is disclosed. [The use of a water-degradable solid polymer that decreases in molecular weight with time is not disclosed.]

FIG. 2 shows a cross-section of a wire-wrapped sand control screen. The screen includes basepipe 130, stand-offs 134 and wire 136. Washpipe or tail pipe 132 is shown inside the screen. The protective coating on the screen is designated 122. It should be understood that a screen is illustrated, but a perforated liner or permeable sintered medium may be protected by a protective coating such as coating 122.

The use of PLA, PHA and other polyester polymers makes possible a timed degradation of the coating, rather than the employment of temperature alone or dissolution in a fluid as disclosed in the '919 Publication. The properties of the polyester may be selected to maintain sufficient mechanical strength to prevent displacement of the polymer from the screen as it is placed in a well. This time may be from several hours to days, depending on the time required to place the coated screen in a well. An example of the decrease in molecular weight of poly (DL-lactide) with time is provided in the paper "Further investigations on the hydrolytic degradation of poly (DL-lactide)," *Biomaterials* 20 (1999) 35-44. The data in the paper were obtained at 37° C. and at 60° C. As can be noted in the U.S. Pat. No. 4,716,964, referenced above, the rate of degradation is much more rapid at temperatures more typical of the temperature in wells. The polymer coating initially should have a melting point higher than the temperature expected in the well. The polymer should degrade to form a material that can be displaced from the well. If the polymer should flow outwardly from the screen, the polymer should not permanently damage permeability of the gravel placed in the well. Some or the entire polymer may be produced from the well as a viscous liquid. The initial strength of the solid polymer should be sufficient to prevent flow across the screen, in the area where the polymer is applied, under pressure differentials across the screen as it is placed in the well. The polymer coating may be used, for example, to prevent flow through only selected areas of the screen as it is put in a well.

To increase initial strength of the polymer, a composite may be formed with the polymer by incorporating particles of a rigid solid, which may be a soluble crystalline material, for example, in the polymer before it is placed on the screen. Polymers having varying degradation rates may be used on different areas of a screen. For example, a more rapidly degrading polymer may be used over the lower portion of a screen.

Degradable polymer, such as PLA, may be applied to the screen, for example, by heating the polymer to allow flow or extrusion and coating the polymer on the finished screen. The screen may be heated before application of the polymer to allow more uniform flow of polymer into the screen. Alternatively, the polymer may be applied from solution in a solvent and the solvent removed to form a solid polymer. Alternatively, the base pipe or mandrel of the screen may be coated and the holes plugged with hot PLA or other water-degradable polymer before the wire of a screen is applied. Alternatively, blank pipe to be run into a well may be coated with the degradable polymer. The degradable polymer may be formulated to contain any or all the additives taught by the '919 Publication. The additives would then be released to enter the fluids around the screen or blank pipe as the polymer degrades.

There are reasons to attach various mechanical devices to the outside of tubulars as they are placed in a well. The devices may be used to measure physical or chemical variables or to modify flow conditions in the well, for example. A change in the position, status or operation of the device after a selected time may be desirable. A degradable polymer, such as PLA or a PHA, may be used to form a mechanical part of the device or a support for the device. The degradation rate of the degradable polymer may be selected to allow the desired change to occur in a selected range of time after placement of the device in a well. For example, FIG. 3 is adapted from U.S. Pat. No. 5,509,474. In this example, tubing **106** has been placed in a well inside casing **12**. The annulus between tubing and casing will ordinarily be filled by an aqueous fluid. Sensors **111** are designed to be released from the vicinity of the outside surface of tubing **106** and then to spring against the inside wall of casing **12**. An electromechanical device could be used to release the spring-loaded sensors. Alternatively, groove **200** may be formed in insulating material collar **114** and the spring-loaded sensors may be held in groove **200** by placing a selected solid water-degradable polymer over the sensor, shown at **111(a)**, in the groove, using techniques of placement such as described above for a screen. After tubing **106** is placed in a well in an aqueous fluid environment, polymer in groove **200** degrades to a range of mechanical properties (determined by the decrease in molecular weight of the degradable polymer) that allows sensor **111** to be released and to spring into the position shown at **111**, which is in contact with the inside surface of casing **12**.

The applications of degradable polymers disclosed herein to allow a timed change in location of a part or parts of mechanical devices can be readily seen by one of skill in the art of each device. The degradable polymer may easily be configured to allow the change to occur as compressive strength of the polymer degrades, as tensile strength degrades, as bending strength degrades, or as a combination of properties changes. The time of change can be determined by selecting a degradable polymer that changes in properties at a rate to allow the change to occur in a desired time range. This range may be hours, days or months, depending on the mechanical configuration and the polymer selected.

In other applications, flow configuration or pressure changes may be desired in a well after a selected time. For example, a port may preferably be opened after a selected time, in the range of hours, days or months. The port may be inaccessible or require expensive operations to open. For example, the port may be used to co-mingle fluid streams being produced from a well and be in an aqueous environment. A plug may be formed from a degradable polymer as disclosed herein. Tests can be performed with different polymer compositions to select the polymer providing the opening of the port in the desired time range and at the pressure differential existing across the port when in the well. Measurements of physical properties of a selected degradable polymer as a function of time and at selected temperatures in an aqueous environment may also be used to predict the time of opening of a selected port under selected conditions. Alternatively, the polymer can be made in the form of a seal or gasket that degrades in time to allow flow. Such measurements and tests should take into account the dimensions of the degradable polymer body that is degrading, since such changes in properties are known to be affected by dimensions of the body, which affect the length of the diffusion path of water molecules into the degradable material and the diffusion path of reaction products from the polymer.

In another embodiment, mechanical devices or selected parts of mechanical devices that are placed in a well may be formed from solid degradable polymer such as PLA or PHA. For example, parts of a packer, a bridge plug or a cement retainer may be formed of water-degradable polymer. After a selected range of time, from hours, to days or months, the device or selected parts of the device may be designed to decrease in properties so as to release the device and facilitate retrieval. Alternatively, the entire device may be formed of a degradable polymer where strength of the polymer is adequate. For example, a nipple or pipe section may be formed of degradable polymer. The nipple or pipe may degrade and later be produced from a well. The pipe may be the "tail pipe" used in a sand control screen, for example.

Whereas the PLA used in fluids is preferably amorphous, as described above, the PLA used in mechanical or flow control devices may be amorphous or crystalline. The bending strength of rods of poly (D-lactide) (PLA) (which would be crystalline) when made by routine injection molding has been measured to be in the range of 40-140 MPA. Rods formed by solid state extrusion had bending strengths up to 200 MPA ("Enhancement of the mechanical properties of polylactides by solid-state extrusion," *Biomaterials* 17, (March, 1996, 529-535). Further information about PLA and its properties is provided in a chapter entitled "Present and Future of PLA Polymers" in the book *Degradable Polymers, Recycling, and Plastics Waste Management*. Ed. by Ann-Christine Albertsson and S. J. Huang, Marcel Dekker, Inc. It is well known that strength may be increased by the use of composites made of the thermoplastic polymer. Where added strength is desired, composite formed from a degradable polymer may be used. PLA, for example, can be molded as other thermoplastic materials are formed or it may be formed by extrusion other processing steps known in industry.

An example of a simple mechanical device that may be formed or partially formed from PLA or other water-degradable polymer is a flotation container to be attached to casing being run into a horizontal well. Such flotation devices made of metal are well known. The walls and ends of such a container may be formed from degradable polymer, with adequate supports of degradable polymer between the ends to prevent collapse, or the ends and supports may be formed of

degradable polymer and designed to allow walls to collapse after a selected time in the well (and before cementing).

Other mechanical parts that may be more easily left in a well than retrieved may also be formed from degradable polymer such as PLA. For example, the case or container of perforating devices may be formed of degradable polymer. After a selected time, the device may then be easily flowed from the well, if desired.

Although the present invention has been described with reference to specific details, it is not intended that such details should be regarded as limitations on the scope of the invention, except as and to the extent that they are included in the accompanying claims.

What I claim is:

1. A method for changing a flow pattern in a well having a casing comprising placing a solid degradable polymer piece in an internal device or internal flow channel in apparatus within the casing in the well such that decrease of a strength of the degradable polymer after a selected range of time causes changing of the flow pattern in the well, wherein the solid degradable polymer piece comprises polylactic acid.

2. The method of claim 1 wherein the solid degradable polymer piece is in the form of a plug, seal or gasket.

3. The method of claim 1 wherein the changing of flow pattern in the well causes co-mingling of fluid streams produced from the well.

4. A method for changing a pressure in a well having a casing comprising placing a solid degradable polymer piece in an internal device or internal flow channel in apparatus within the casing in the well such that decrease of a strength of the degradable polymer after a selected range of time causes changing of the pressure in the well, wherein the solid degradable polymer comprises polylactic acid.

5. The method of claim 4 wherein the solid degradable polymer piece is in the form of a plug, seal or gasket.

6. A method for changing a flow pattern or pressure in a well having a casing comprising placing a solid hydrolytically degradable polymer piece in an internal device or internal flow channel in apparatus within the casing in the well such that decrease of a strength of the degradable polymer after a selected range of time causes changing of the flow pattern in the well, wherein the solid degradable polymer is chemically degraded to polymers having shorter chains that are water soluble.

7. The method of claim 6 wherein the solid degradable polymer piece is in the form of a plug, seal, or gasket.

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