



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

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<b>(21) International Application Number:</b> PCT/NO93/00173 <b>(22) International Filing Date:</b> 19 November 1993 (19.11.93)  <b>(30) Priority Data:</b> 924493                      20 November 1992 (20.11.92)    NO  <b>(71) Applicant (for all designated States except US):</b> SINVENT A/S [NO/NO]; N-7034 Trondheim (NO).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> JUSTNES, Harald [NO/NO]; Asbjørnsensgt 36, N-7015 Trondheim (NO). DAHL-JØRGENSEN, Einar [NO/NO]; Buengv. 93, N-7079 Flatåsen (NO).  <b>(74) Agent:</b> GRÆSBØLL, Sigrun, E.; Bryn & Aarflot A/S, P.O. Box 449 Sentrum, N-0104 Oslo (NO).	<b>(81) Designated States:</b> BR, CA, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>	
<b>(54) Title:</b> ALTERNATIVE CEMENTING MATERIALS FOR COMPLETION OF DEEP, HOT OIL-WELLS		
<b>(57) Abstract</b> <p>A cementing material with controlled curing time, for use in the primary and secondary cementing of deep hot oil wells with a static background temperature in the range of 120-200 °C, comprising a) a resin consisting of ortho-, meta- and/or para-diallyl phthalates and/or prepolymers and/or oligomers thereof; b) a curing agent in the form of a dissolved organic peroxide generating free radicals; and, c) an inhibitor for stabilizing free radicals so as to obtain the required open time for pumping the resin in place, and optionally the following: d) one or more heavy weight filler(s) for controlling the density of the cement; e) extender materials controlling the consistency, and f) materials compensating inherent shrinkage.</p>		

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Alternative cementing materials for completion of deep, hot  
oil-wells

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5 An alternative material to cement-water slurries has been  
developed for the completion (primary and secondary  
cementing) of deep, hot oil wells with a static background  
temperature in the range of 120 - 200°C (248 - 392°F).

10 The binder in the new, alternative material is based on a  
diallyl phthalate resin with the setting/curing time  
controlled by the addition of a temperature sensitive  
peroxide initiator and a suitable inhibitor. In addition,  
mineral fillers acting as weighting materials (density  
controlling agents) and extenders (to minimize the resin  
15 content) may be included.

High temperatures may in general cause problems in  
controlling the curing time of traditional cement-water  
slurries, where the proportioning of retarders is a delicate  
20 balance between flash setting and over-retardation resulting  
in unacceptable waiting-on-cement (WOC) times. The curing of  
a diallyl phthalate resin is more easy to control. In  
addition, unlike cement-water slurries, the new resin may be  
premixed with all components on-shore and stored for a  
25 longer period prior to the cementing job. This is possible,  
since it is the temperature in the well bore that activates  
the resin.

30 Furthermore, primary cementing may be difficult in wells  
that have been drilled such that they deviate substantially  
from a vertical position, or where part of the well is  
horizontal. Gravity may cause segregation of cement  
particles from the water phase in cement-water slurries,  
creating non-solidified channels along the casing or liner.  
35 In the new, alternative material, the liquid phase is the  
binder. Thus, in the event of segregation of weighting  
materials or extenders, the possibility of non-solidified  
channel formation can be eliminated since the liquid itself  
becomes a solid upon curing.

The new, alternative cementing materials may have additional advantages compared to cement-water slurries when the possibility of gas-migration is present. With a proper selection of initiator, a "right angle" set may be obtained  
5 for the resin. This will lead to a very short time gap for the transition from liquid to solid. Furthermore, the material has no open porosity (unlike cement-water slurries), which will further limit the possibility of gas intrusion.

10

There are also secondary cementing operations where a filled or unfilled resin may be used as a cost-efficient material. Such an operation may be squeeze cementing used in oil wells for the following purposes: (1) repairing micro-annulus  
15 formed in the primary cement causing leaks between formation zones, (2) correcting defective primary cement jobs, (3) isolation of abandoned pay zones and (4) temporary isolation of one reservoir formation in a multiple production zone well while producing the other to depletion.

20

Two cases of resin based cementing materials for geothermal well bores are known from the literature:

The first system (Zeldin, A.N., Kukacka, L.E. and Carciello, N: "New, Novel Well-Cementing Polymer Concrete Composite",  
25 American Concrete Institute (ACI), Special Publication 69: "Application of Polymer Concrete", 1981, part 69-5, pp. 73-92) is based on a resin with initiator and inhibitor. However, unlike the present invention, the complete curing  
30 of this resin depends on the presence of water. Furthermore, the main component of the resin is organic siloxanes, which are far from the present system based on diallyl phthalates.

The second system (Eilers, L.H.: "Process for cementing geothermal wells", United States Patent 4,556,109, 1985-12-03, 3 pp.) is based on a completely different resin curing  
35 according to a condensation mechanism, rather than a free radical polymerization such as for the resin in the present invention. The main component of that resin is furfuryl

alcohol/furfural with a zinc accelerated, acid catalyzed curing.

5 The resin of the new, alternative cementing material is characterized by consisting of diallyl phthalates and prepolymers/oligomers thereof. All three isomers of diallyl phthalate are included in the invention; ortho- (or 1,2-), meta- (or 1,3- or iso-) and para- (or 1,4- or ter-) diallyl phthalate. The amount of diallyl phthalates in the  
10 formulation is 20 - 99 % by weight.

Furthermore, the resin is characterized by being cured due to the thermal decomposition of a dissolved organic peroxide generating free radicals. Examples of such organic peroxides  
15 are di-tert-butyl-peroxide, tert-butyl-hydroperoxide and 2,5-bis(tert-butyl peroxy)-2,5-dimethylhexyne-3. The dosage of initiator required for a proper curing is 0.1 - 5 % by weight of the resin.

20 Finally, the required open time (pot life) for pumping the resin in place is obtained by dissolving a suitable inhibitor stabilizing free radicals. An example of such an inhibitor is para-benzoquinone (PBQ). The amount of inhibitor required depends on the temperature and the type  
25 of initiator used, but should be within the range 0.02 - 2 % by weight of the resin.

The density of the resin may be controlled by adding a heavy weight filler (weighting material). Finely divided hematite  
30 ( $\text{Fe}_2\text{O}_3$ ) is preferred, but other materials such as baryte ( $\text{BaSO}_4$ ) and ilmenite ( $\text{FeTiO}_3$ ) may be applicable as well.

The consistency of the resin may be controlled by adding an extender. Finely divided calcite ( $\text{CaCO}_3$ ) is preferred, but  
35 silica flour and condensed silica fume ( $\text{SiO}_2$ ) may be used as well.

The inherent shrinkage of the resin during curing may be compensated by adding bentonite predried at a temperature

just below the circulation temperature of the application range in the well bore.

The following examples are meant to illucidate the invention  
5 without limiting it.

**Example 1: Open time for a DAP resin as a function of static background temperature**

10 A resin was made from 100 g ortho-diallyl phthalate (DAP), 30 g DAP prepolymer, 1 g tert-butyl-hydroperoxide and 0.45 g para-benzoquinone. The homogeneous liquid was placed in a 25 ml volumetric flask, which was placed in a silicone oil bath with a static temperature of 150°C (302°F). The  
15 temperature vs time was measured for both the resin and the bath. Figure 1 shows the temperature profile of the surrounding (oil-bath) and the DAP-resin cured at 150°C. Apparently, the exothermic curing reaction started at 152 min, while the curing peak came after 243 min with a heat  
20 exotherm of 12°C.

Experiments identical to the preceding one were performed with static background temperatures of 131, 141, 150, 160 and 171°C, respectively. According to kinetics, the relation  
25 between the natural logarithm of the inverse of pot life (t),  $\ln(1/t)$ , and the inverse of the absolute temperature (T) in °K,  $1/T$ , should be linear. Figure 2 shows that this is valid for the DAP resin, and reveals the linear pot life (t) vs temperature (T) relation for the DAP resin. Thus,  
30 such linear relations may be used to find the pot life of a spesific resin at a given temperature by interpolation.

**Example 2: Open times for an iso-DAP resin as a function of static background temperature**

35 A resin was made by mixing 100 g meta-diallyl phthalate (iso-DAP) with 1 % 2,5-bis(tert-butyl peroxy)-2,5-dimethyl-hexyne-3 and 0.80 % para-benzoquinone (PBQ), by weight of the resin. The homogeneous liquid was placed in a 25 ml

volumetric flask, which was placed in a silicone oil bath with a static temperature of 150°C (302°F). The temperature vs time was measured for both the resin and the bath, as revealed in Figure 3, showing the temperature profile of the surroundings (oil-bath) and the iso-DAP resin cured at 150°C. Apparently, the exothermic curing reaction started at 140 min, while the curing peak came after 155 min with a heat exotherm of 55°C.

Experiments identical to the preceding one were performed with static background temperatures of 131, 141, 150, 160 and 171°C, respectively, for resins with PBQ dosages of 0.2, 0.4, 0.6 and 0.8 % by weight of the resin. According to kinetics, the relation between the natural logarithm of the inverse of pot life ( $t$ ),  $\ln(1/t)$ , and the inverse of the absolute temperature ( $T$ ) in °K,  $1/T$ , should be linear. It is apparent from Figure 4, which shows the linear pot life ( $t$ ) vs temperature ( $T$ ) relations for iso-DAP resin with different dosages of inhibitor PBQ, that this is valid for the iso-DAP resin as well, and for all the investigated PBQ dosages. Thus, these linear relations may be used to find a suitable resin composition for a required open time at a given temperature by interpolation.

**Example 3: The effect of pressure on the open time for iso-DAP resin**

An iso-DAP resin was made as described in Example 2. The curing chamber was now a high temperature - high pressure (HTHP) viscometer after the viscometer parts had been removed. The curing of iso-DAP resin was carried out at 1, 500 and 900 bars, respectively, and the end temperature was set at 150°C. All samples were taken from the same batch in order to exclude concentration variations. The temperature vs time profiles for the iso-DAP resin at different pressures when the end temperature was set at 150°C are shown in Figure 5.

Initially, the effect of the pressure was difficult to see correctly, since the temperature vs time profile varied for each experiment. In order to correct for this, the activation energy for the resin was calculated. The slope of the linear relation in Figure 4 gives  $E_a/R$  for the resin, where  $E_a$  is the activation energy and  $R$  is the gas constant (8.3144 J/mole·°K), according to reaction kinetics. In this way,  $E_a$  was found to be 185,326 J/mole. This value was used in a maturity function in order to calculate the equivalent time at 150°C from the experimental curing time at variable temperature vs time profile in the elevated pressure experiment with the HTHP viscometer. The results are revealed in Table 1 and Figure 6, which figure shows open time and equivalent open time at 150°C as a function of pressure for the iso-DAP resin. It should be noted that the exact pot life of the 2071 resin at 1 bar was difficult to determine, since the exotherm is not as distinct as at higher pressures. Thus, the experiment at 1 bar was repeated.

20

Table 1. Open time (min) and equivalent open time at 150°C (min) for the iso-DAP resin as a function of pressure.

25

	TIME	EQUIVALENT TIME
1	101	72,45
1	139	76,00
500	121	82,00
900	105	69,00

30

35

40

The experiments in the HTHP viscometer revealed that the exothermic peak increased with increasing pressure, viz., 40, 110 and 125°C at 1, 500 and 900 bars, respectively, and that increasing pressure also improved the "right angle" set (see Figure 5). However, increasing pressure did not seem to change the equivalent open time of the iso-DAP resin significantly (see Table 1 and Figure 6). This information is vital for the utilization of the iso-DAP resins in deep well bores (i.e. high pressures).

**Example 4: Shrinkage compensation and compressive strength of mineral filled iso-DAP resin**

Tests with an iso-DAP resin filled/weighted with calcite/-hematite, and using bentonite pre-dried at 150°C as a shrinkage compensator, were performed at 150°C and both 10 and 900 bars pressure in the chamber of a High Temperature-High Pressure (HTHP) viscometer (viscometer part removed). The resin was contained in a glass cylinder surrounded by oil, and the temperature vs time was recorded by a thermocouple in the oil and one in intimate contact with the glass wall of the cylinder. The composition of the complete iso-DAP resin was:

25	Iso-DAP with 2 % 2,5-bis(tert-butyl peroxy)- -2,5-dimethylhexyne-3 and 0.7 % para-benzoquinone.....	285 g
	Calcite filler (lime stone).....	513 g
	Hematite (fine).....	256 g
	Bentonite (pre-dried at 150°C).....	29 g
30		-----
		TOTAL = 1083 g

The above recipe will give a calculated fresh density of 2.11 g/cm<sup>3</sup>. Note that the high content of initiator in this case (usually 1 %) gave a shorter open time than the usual 2 h at 150°C, since it is the initiator/inhibitor ratio that determines the open time. However, in this example only the shrinkage and the compressive strength of the samples were of interest.

The shrinkage of the samples was calculated by the difference in density in the fresh and in the cured state. The fresh density was measured by a graduated glass cylinder (volume and weight) to  $\rho_f = 2.124 \text{ g/cm}^3$ . The density of the cured resin was calculated by weighing the whole sample (after removing the glass container) in air ( $m_a$ ) and when immersed in water ( $m_w$ );

$$\rho_c = m_a \cdot 1.00 \text{ g/cm}^3 / (m_a - m_w)$$

The densities of the samples cured at 10 and 900 bars were 2.21 and 2.15  $\text{g/cm}^3$ , respectively.

Note that the sample cured at 900 bars had a well defined heat profile curve (maximum difference compared to bath about  $40^\circ\text{C}$ ), while the temperature in the sample at 10 bars only was slightly different ( $<4^\circ\text{C}$ ) from the ambient temperature of  $150^\circ\text{C}$ , which comply well with the results in Example 3.

The shrinkage of the two samples cured at 10 and 900 bars were then calculated to 3.89 and 1.21 %, respectively, by means of the following equation:

$$\text{Shrinkage} = (\rho_f / \rho_c - 1) \cdot 100 \%$$

The compressive strengths of the corresponding samples were determined to 52.6 and 59.2 MPa, respectively.

The results demonstrate the effectiveness of pre-dried bentonite as a shrinkage compensator. Pre-drying bentonite to just below the expected circulation temperature makes it a versatile shrinkage compensator for resin systems over a wide range of temperatures.

## PATENT CLAIMS:

1. A cementing material with controlled curing time, where the time before the curing starts ("pot life") is more than one hour, for use in the primary and secondary cementing of deep hot oil wells with a static background temperature in the range of 120-200°C and with a pressure up to 1500 bar, characterized in that it comprises
- a) a resin consisting of ortho-, meta- and/or para-diallyl phthalates and/or prepolymers and/or oligomers thereof;
  - b) a curing agent in the form of a dissolved organic peroxide generating free radicals by thermal decomposition; and
  - c) an inhibitor for stabilizing free radicals so as to obtain the required open time (pot life) for pumping the resin in place, and optionally the following
  - d) one or more heavy weight filler(s) (weighting materials) for controlling the density of the cement;
  - e) extender materials controlling the consistency, and
  - f) materials compensating inherent shrinkage.
2. The cementing material of claim 1, characterized in that the amount of diallyl phthalates in the formulation is 20 - 99 % by weight.
3. The cementing material of claim 1, characterized in that the organic peroxide is di-tert-butyl-peroxide, tert-butyl-hydroperoxide or 2,5-bis(tert-butyl peroxy)-2,5-dimethylhexyne-3, and is present in an amount of 0.1 - 5.0 % by weight.
4. The cementing material of claim 1, characterized in that the inhibitor is para-benzoquinone (PBQ), and is present in an amount of 0.02 - 2 % by weight.
5. The cementing material of claim 1, characterized in that the heavy weight filler (weighting material) is finely divided hematite ( $\text{Fe}_2\text{O}_3$ ), baryte ( $\text{BaSO}_4$ ), or ilmenite ( $\text{FeTiO}_3$ ).

6. The cementing material of claim 1, **characterized in that** the extender material is finely divided calcite ( $\text{CaCO}_3$ ), silica flour or condensed silica fume ( $\text{SiO}_2$ ).

5

7. The cementing material of claim 1, **characterized in that** the material compensating the inherent shrinkage of the resin during curing is bentonite pre-dried to just below the circulation temperature in the well bore, in an amount lower than 30 % by weight of the resin.

10

1121-RESIN CURED AT 150°C

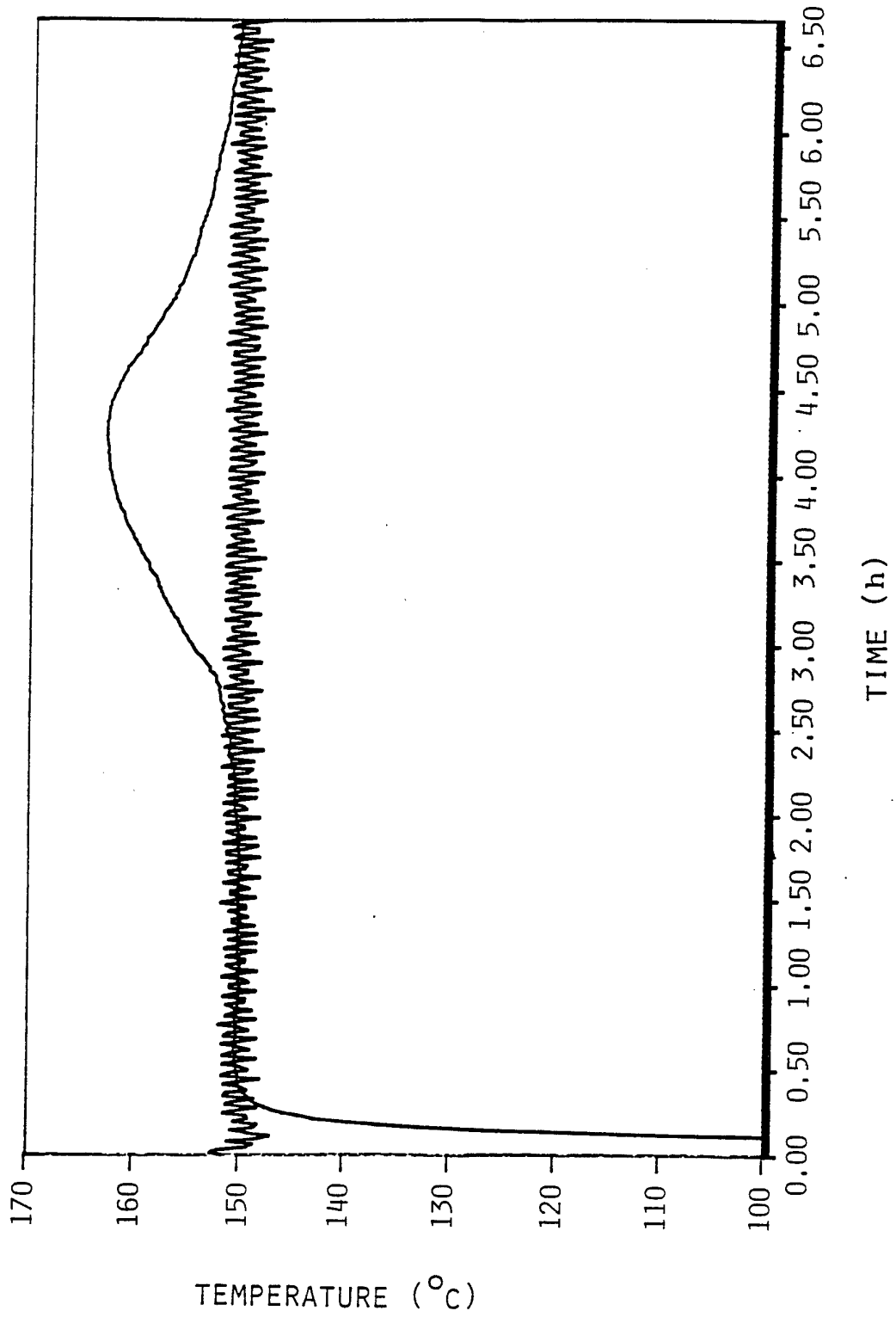


FIG. 1  
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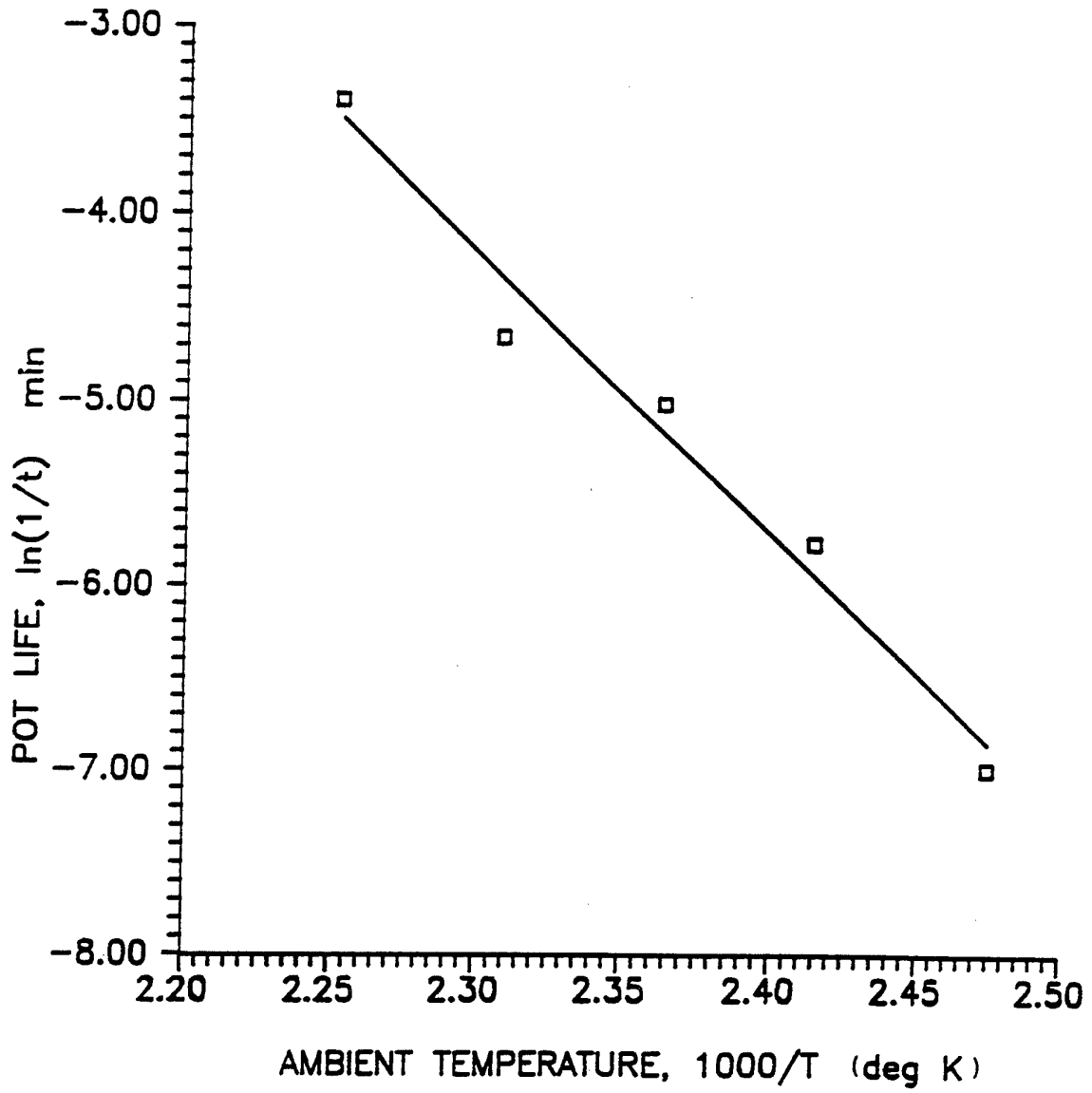


FIG. 2

SUBSTITUTE SHEET

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CURING RESIN 2071 AT 150°C  
1% INITIATOR 7, 0.8% INHIBITOR 1

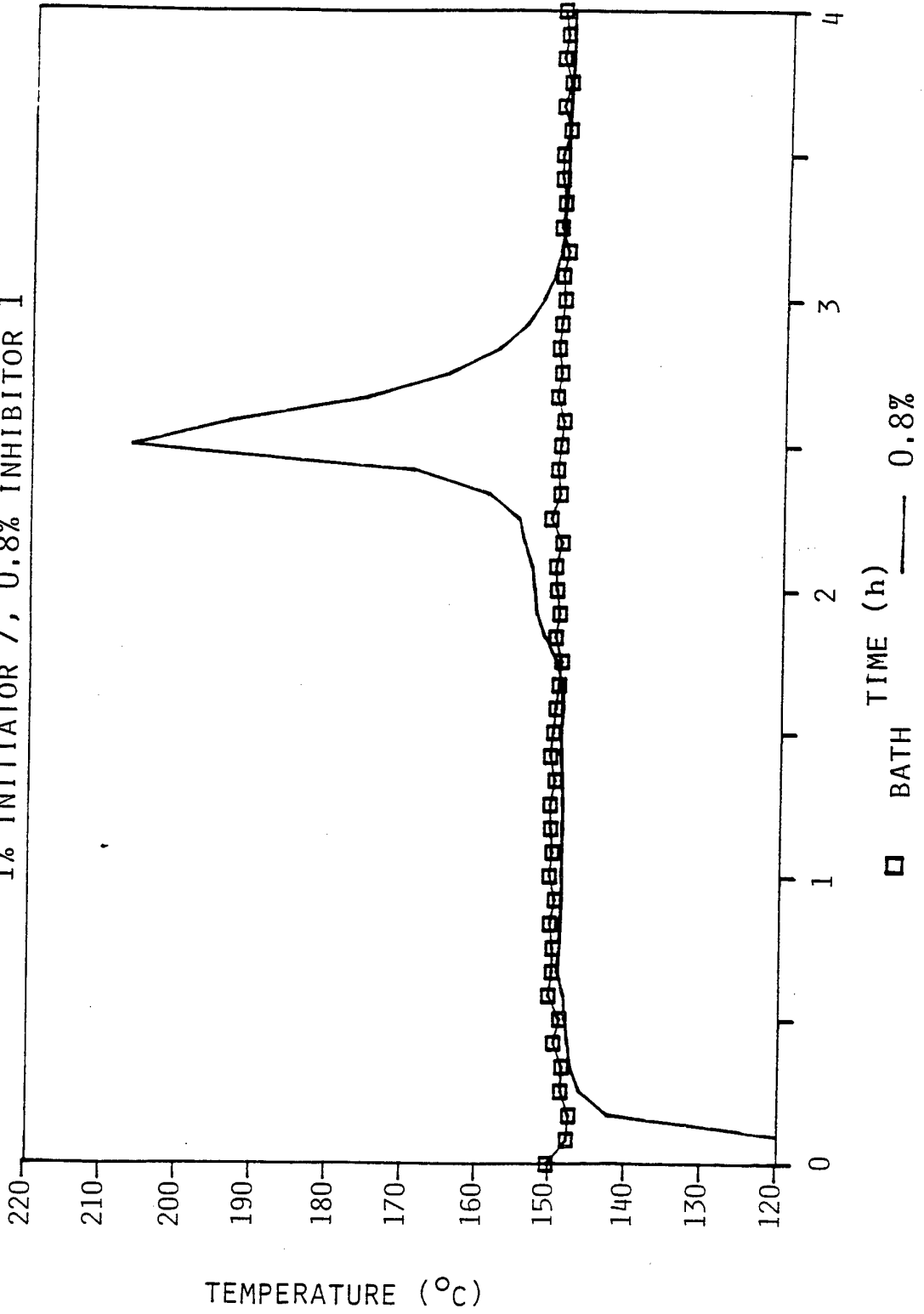


FIG. 3  
SUBSTITUTE SHEET

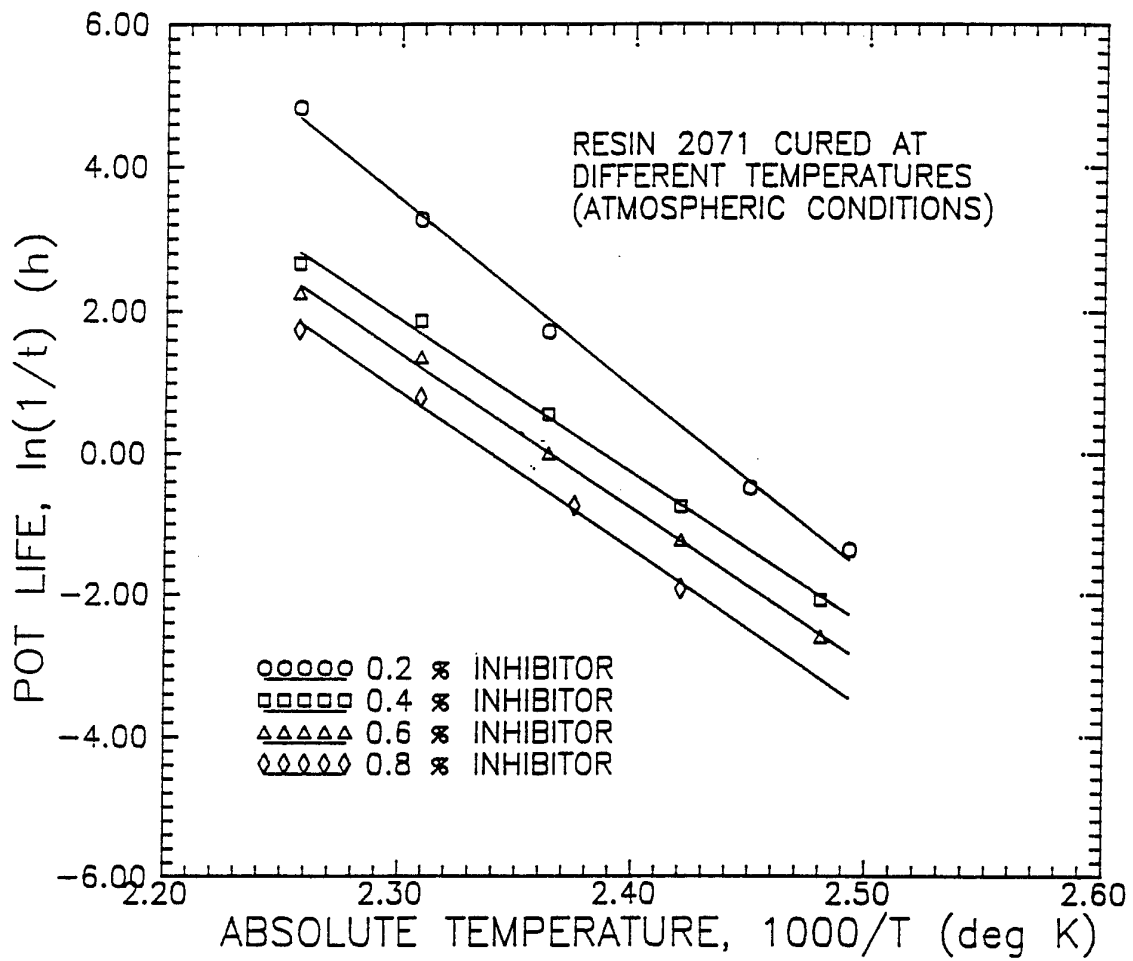


FIG. 4

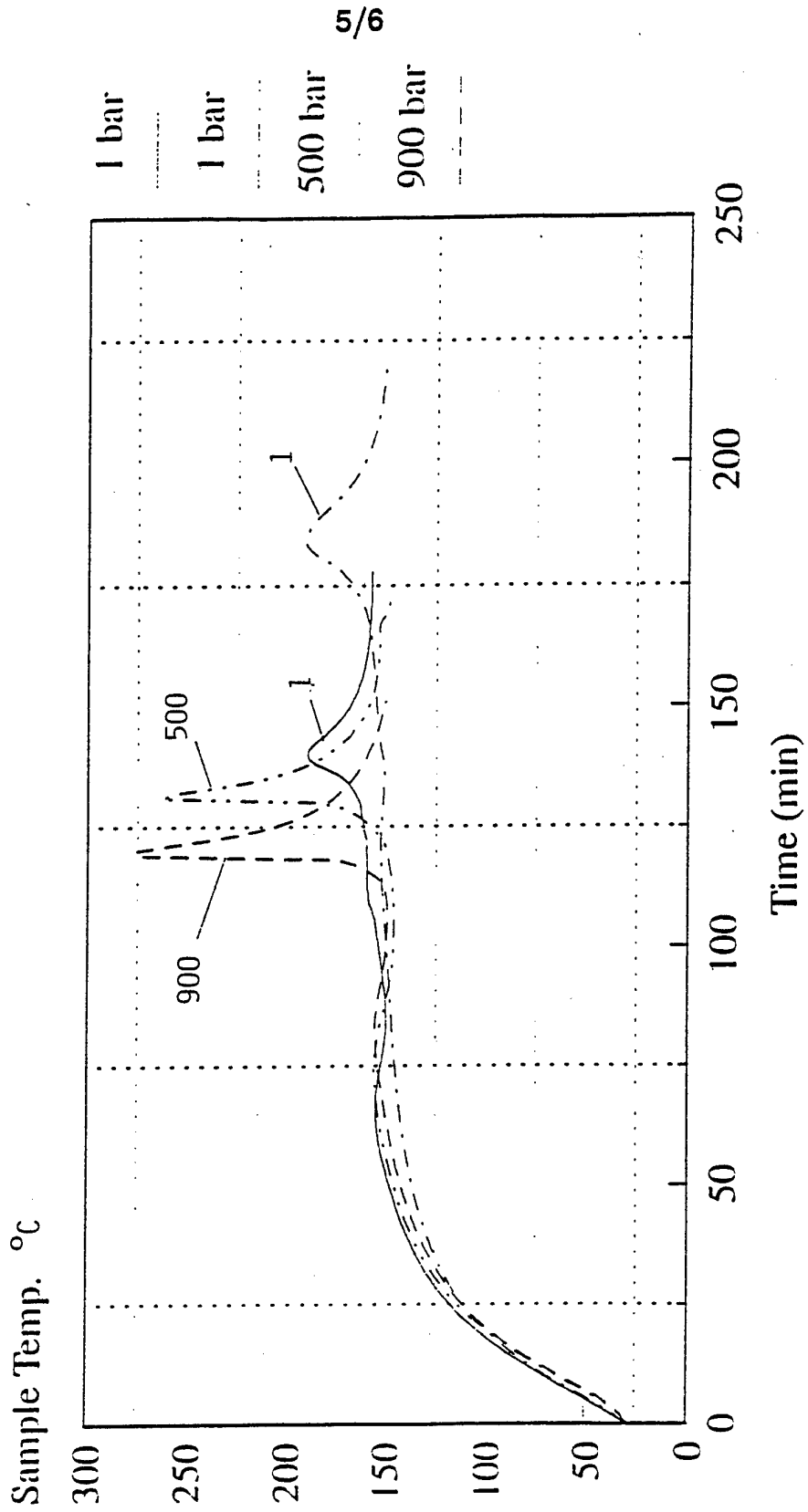


FIG. 5

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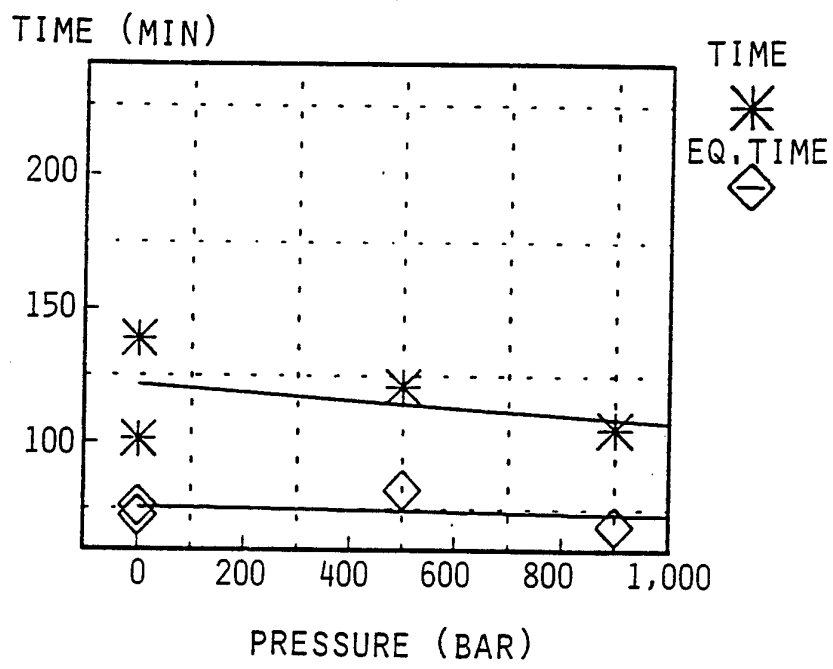


FIG. 6

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/NO 93/00173

<b>A. CLASSIFICATION OF SUBJECT MATTER</b>		
IPC5: C04B 26/18, E21B 33/13 According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b>		
Minimum documentation searched (classification system followed by classification symbols)		
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<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Dialog Information Services, File 350, World Patent Index 63-80, Dialog accession no. 001434167, WPI accession no. 75-83910W/51, OSAKA SODA KK: "Injection moulding compsn.-based on poly (diallyl isophthalate) and poly (diallyl phthalate) prepolymer blends". JP 50078638, A, 750626, 7551 (Basic)	1,2,7
A	CA, A, 1247352 (FRIEDMAN, ROBERT H.), 28 December 1988 (28.12.88), page 3, line 31 - page 4, line 4	1-7
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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

30/12/93

International application No.  
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CA-A- 1247352	28/12/88	NONE	
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