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MASTER

CHEMICAL TEMPERATURE INDICATORS FOR
GEOTHERMAL APPLICATIONS

FINAL REPORT

J.V. Gaven, Jr., C.S. Bak, V.V. Jones & B. Grow

✓ SPECTRO-SYSTEMS, INC.
8000 FORBES PLACE
SPRINGFIELD, VIRGINIA 22151

951 1181

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I. ABSTRACT

The objective of this program was the development of a simple, reliable method for temperature measurement in geothermal wells during drilling operations. The method of choice involves the use of a series of "chemical temperature indicator" materials, with sharply defined melting temperatures over the temperature range $80^{\circ}\text{C} \leq T \leq 350^{\circ}\text{C}$. The temperature indicator materials are exposed to the geothermal environment of interest and subsequently visually examined. Those indicators which have undergone the solid to liquid phase transition associated with melting are readily distinguishable from unmelted indicators, thereby allowing maximum exposure temperature to be bracketed between the melting temperatures of 2 adjacent members of the temperature indicator series.

Following an extensive literature search, the most promising candidate temperature indicator materials were selected for laboratory experimentation. Differential Scanning Calorimeter measurements were used to determine normal melting point, sharpness of melting point and heat of fusion of the candidate materials. As a result of these experiments, 42 alloys and 9 organic compounds were demonstrated to be acceptable temperature indicators. Since 7 organics had melting temperatures close to corresponding alloys, the useful series of temperature indicators is comprised of 44 materials.

Experiments were carried out to develop a configuration for the indicators compatible with direct addition to drilling muds. Preliminary experimentation was performed on stress resistance and hydrodynamic characteristics of the indicator configuration.

The temperature indicators can be made in production quantities at an average cost of \$1.00/each or less.

Recommendations are made for testing the indicator configurations at elevated pressures in drilling fluid and for carrying out full scale field testing of the indicators under a variety of geothermal conditions.

II. INTRODUCTION

The objective of this program was the development of a simple, reliable method for temperature measurement in geothermal wells during drilling operations. The method of choice involves the use of a series of "chemical temperature indicator" materials, with sharply defined melting temperatures over the temperature range $80^{\circ}\text{C} \leq T \leq 350^{\circ}\text{C}$. The temperature indicator materials are exposed to the geothermal environment of interest and subsequently visually examined. Those indicators which have undergone the solid to liquid phase transition associated with melting are readily distinguishable from unmelted indicators, thereby allowing maximum exposure temperature to be bracketed between the melting temperatures of 2 adjacent members of the temperature indicator series.

The original concept involved the addition of the temperature indicators to circulating drilling fluid. For example, if the anticipated temperature of interest were, $125^{\circ}\text{C} \leq T \leq 175^{\circ}\text{C}$, only those materials melting within that range would be employed. The materials would circulate down the drill string, through the orifices in the drill bit and return to the surface with the drilling fluid. Recovery of the temperature indicators is effected on or near the shale shaker. Those indicators which had been exposed to temperatures at or above their melting temperatures, and had melted and resolidified would be readily distinguishable by visual inspection, from those which were unmelted.

The original concept described above remains viable. In addition, several other geothermal temperature measurement applications have become evident during the course of this program. Successful field testing of the indicators, however, remain to be demonstrated.

The initial phase of the program involved a survey of the state of the art in geothermal temperature measurement, the collection and critical analysis of thermochemical and associated data, and the generation of a computer program for efficient exercise of the data base. Phase 1 was successfully completed and the results reported (1).

Phase 2 of the program is the subject of this report. Phase 2 involved laboratory experimentation on the most promising candidate temperature indicator compounds. Differential Scanning Calorimeter measurements were used to determine normal melting point, sharpness of melting point and heat of fusion of the candidate materials. Experiments were carried out to develop a configuration for the indicators compatible with direct addition to drilling muds. Preliminary experimentation was performed on stress resistance and hydrodynamic characteristics of the indicator configuration.

Phase 2 culminated in a laboratory demonstration of the complete series of indicator materials. In addition, a preliminary cost estimate for the indicators in production quantities was made, and a program plan generated for a proposed Phase 3, involving field testing of the indicators in a variety of geothermal environments.

This report is organized as follows. The following section, which is the bulk of the report, describes experimental procedures and results. In the next section a preliminary cost estimate for the temperature indicators in production quantities is presented. Following a list of conclusions, recommendations are made for additional work. The final section contains literature citations.

III. EXPERIMENTAL PROCEDURES AND RESULTS

A. THERMAL MEASUREMENTS

The selection criteria for candidate materials and the initial list of selections resulting from the Phase I program have been described in detail elsewhere (1). The thermal properties of candidate materials which are of most interest to this program are the actual melting temperature of commercially available materials (as opposed to Handbook values), breadth of melting temperature range, heat of fusion, and density change upon melting (2).

The first three of the thermal properties listed above were measured with a Differential Scanning Calorimeter (DSC), Perkin-Elmer Model DSC-1B. Temperature readings were calibrated using the melting points of pure Indium (156.60°C), Tin (231.88°C) and Lead (327.47°C) as standards. Samples of candidate compounds, typically on the order of 5-6 mg., were placed in Aluminum sample pans, and weighed to ± 10 micrograms on a Perkin-Elmer Autobalance, Model AD-2. The DSC sample chamber was purged with a constant flow of dry nitrogen at 20 cc/minute. Measurements were recorded with a Hewlett-Packard Model 83 strip chart double-pen recorder; one pen was used for the DSC thermal trace and the other for temperature marking.

DSC results for organic compounds and metallic alloys and analysis of the recorded thermal curves are discussed separately below.

1. Organic compounds

In addition to the 23 organic compounds selected in Phase I (1), a further search was made for candidate materials. Ultimately, 42 organic compounds were selected and procured (3). The DSC measurements showed, however, that only 9 compounds had acceptable properties for use as temperature indicator materials. The remaining compounds were rejected due to sublimation, decomposition or too broad a melting range. Figure 1 shows typical heat absorption curves for good and poor (unacceptable) organic compounds. For heavily sublimating materials, the absorption curve becomes irregular over a wide temperature range as shown in Fig. 2.

The list of finally accepted organic compounds will be combined with acceptable metallic alloys and presented below in Table 1.

2. Low-Melting Alloys

Several lead-tin binary alloys of various compositions were studied with the DSC to test the sharpness of the melting range. The eutectic mixture of 61.9 wt.% Sn-38.1% Pb melts sharply as expected. However, alloys which have compositions far removed from both the eutectic point and the pure metals exhibit broad melting temperature behavior due to phase separation, even though the samples were prepared by rapid quenching from a homogeneous melt. Consequently, acceptable alloys having sharp melting points are limited to eutectic mixtures of binary, ternary or, in general, multicomponent metal systems.

Good Candidate

Diphenyl Carbonate

MP 77°C

Melting Range <0.1

Poor Candidate

1,2,3,4-Tetrahydrocarbazole

MP 118°C

Melting Range 1.8°C

Fig. 1 DSC CURVES FOR GOOD AND POOR ORGANIC COMPOUNDS

Fig. 2 EXAMPLE OF DSC CURVE FOR ORGANIC COMPOUND WHICH SUBLIMATES

Figure 3 shows typical examples of sharp melting for a eutectic mixture and unacceptably broad melting for a composition somewhat removed from a eutectic point.

Properties of candidate low-melting alloys were reviewed using the excellent data sources "Constitution of Binary Alloys" and its several supplements (4,5,6). About 800 binary phase diagrams were carefully reviewed. In addition, an intensive data search for pertinent alloy compositions and melting points was conducted at the Alloy Data Center, National Bureau of Standards. With the cooperation of Alloy Data Center personnel and access to the computerized data bank and vast literature resources, quite a thorough search was conducted over known alloy compositions and melting points.

Simple forms of metallic alloys that exhibit sharp melting are pure metals, or binary or ternary eutectic mixtures where two (or three) liquidus curves meet at the lowest temperature as shown in Figures 4 and 5. If the liquidus curve is close to the solidus curve, as in the lead-rich phase in Fig. 4, one can also prepare non-eutectic alloys having sharp melting points.

Use can also be made of the sharp melting property of pseudo-eutectic mixtures of metal and intermetallic compounds. For example, Lead forms a pseudo-eutectic point at 311°C with Ag₃Sn (See Fig. 6) in addition to the Pb-Ag-Sn ternary eutectic at 180°C.

In all, 98 alloy compositions were selected and prepared in sealed glass tubing inside a muffle furnace. As a result of DSC study, 42 of these were shown to be acceptable temperature indicator materials. The thermal analysis will be discussed below.

3. Thermal Analysis and Results

Three thermal properties, broadness of the melting range, melting point, and heat of fusion were measured for all candidate materials from the heat absorption curves obtained from DSC measurements. Broadness of the melting range and the melting point were measured as described below.

Since the DSC operates at a constant heating rate, typically 2.5°C/minute, and there is an intrinsic heat conduction lag from heater to sample, the heat absorption curves show an apparent non-zero melting range even for the ultra-pure standard metals used to calibrate the equipment (See Fig. 7). The apparent melting range also depends on the quantity of the sample. These effects were taken into account as follows to obtain the true melting range of the candidate materials. For a given setting of DSC sensitivity and recorder chart speed, the heat of fusion, represented by area A under the heat absorption curve, is related to the apparent melting range $\Delta T'$ and the curve peak h as follows:

$$A \approx 1/2 \Delta T' h \quad (1)$$

A common heat conduction lagging for any DSC run gives rise to the same slope of the absorption curves (7), hence $h \propto T'$. Consequently A is related to $(\Delta T')^2$ by a common constant γ :

$$\gamma = \frac{(\Delta T')^2}{A} \quad (2)$$

Fig. 3 DSC CURVES FOR EUTECTIC AND NON-EUTECTIC COMPOSITIONS

FIG. 4 TIN-LEAD PHASE DIAGRAM

Bi-Cd-Sn
MP 103°C

FIG. 5 TIN - BISMUTH - CADMIUM PHASE DIAGRAM

Fig. 117. Isotherms of liquidus surfaces in the lead corner of the Lead-Silver-Tin system.
(According to EARLE).

FIG. 6 EXAMPLE OF PSEUDO-EUTECTIC

DSC Curve for Standard Metals.

In.

He

Sn.

Sn

R4

2.5°/min
1mV/div
2"/min

2.5°/min
1mV/div
2"/min

100

250

FIG. 7 DSC CURVES FOR CALIBRATION STANDARDS

For standard In, Sn and Pb metals experimentally studied:

$$\eta = 0.62 \pm 0.06 \quad (3)$$

These results confirm that η is reasonably constant. A for tin was found to be almost 3 times greater than that for lead in our samples. Thus, for any candidate material with heat absorption A, the observed melting range, ΔT_{ob} , must be corrected by the apparent range $\Delta T' = \sqrt{A\eta}$ to obtain the true melting range ΔT :

$$\Delta T = \Delta T_{ob} - \sqrt{A\eta} \quad (4)$$

Enthalpies of fusion were measured from the same DSC thermal absorption curves. The DSC was calibrated with the enthalpies of fusion of Indium (6.80 cal./g.), Tin (14.45 cal./g.) and Lead (5.50 cal./g.). These data, together with density changes upon melting, were used to estimate the effect of pressure on melting temperatures, as discussed in the following section.

B. EFFECT OF PRESSURE ON MELTING TEMPERATURE

The effect of pressure on melting temperature was estimated for metal-alloy systems using the following approximate form of the Clapeyron equation (2):

$$\frac{\Delta T}{\Delta P} = \frac{T \Delta V}{\Delta H} \quad (5)$$

where: T = equilibrium temperature,

P = equilibrium pressure,

ΔH = specific enthalpy difference, $H_{liquid} - H_{solid}$ (latent heat)

ΔV = specific volume change, $V_{liquid} - V_{solid}$.

The specific volume changes for pure metals were taken from the literature (8), while the specific volume changes for alloys were estimated from a linear relation of constituent components (9).

The melting point increases (negative sign for a decrease) at high pressure were calculated in units of °C per 1000 psi. For pure metals and alloys, changes in melting temperature are typically on the order of a few tenths of a degree C per 1000 psi pressure. As a result, the list of candidate alloys arranged in order of normal melting point was preserved in the same order at high pressure (e.g. 5000 psi, which is approximately equivalent to 10,000 ft. well depth).

For organic candidate materials, similar estimates can be carried out only semiquantitatively, since few data are available on density and volume change upon melting. If we assume, for a trial, a density of approximately 1 g/cm³, and a 10% volume change upon melting (10), and using the experimental melting point and latent heat data measured with the DSC, the pressure effect in organic materials appears to be several times greater than in alloys. However, this prediction is only qualitative because material properties are

expected to differ widely from organic to organic. The melting point at high pressure can best be determined experimentally in high pressure laboratory equipment (2). Even if it develops that the organic melting temperatures are overly sensitive to pressure, 7 alloys are available as alternatives to the organics.

C. LISTING OF TEMPERATURE INDICATOR MATERIALS

A final listing of candidate materials for Phase 2 is presented in Table 1. The first column shows the alphanumeric marking assigned to each indicator. Such markings will be die-stamped on configuration packages for easy identification of the particular indicator. The brackets indicate alloy system alternatives to the corresponding organics. The remaining columns show experimentally determined melting temperatures and melting ranges, and estimates of the effect of pressure on melting temperature.

To summarize the final listing of candidate materials, 51 compounds have been selected. These consist of 42 metals or alloys and 9 organic compounds. Every organic except two has an alloy alternative. The total number of discrete melting points, counting an alloy-organic pair as one, is 44. Temperatures below 170°C are well covered, with temperature intervals being about 10°C, as originally desired. For temperatures above 170°C, there are two major temperature gaps; one between 329°C and 344°C (15°C interval), and the other 184°C to 198°C (14°C interval). The particular importance of these two temperature ranges in geothermal applications will await determination by field experimentation. Except for the two temperature bands noted above, the coverage over the remainder of the temperature range appears to be reasonably good.

D. STUDY OF TEMPERATURE INDICATOR CONFIGURATIONS

Several different configurations for the temperature indicators have been developed for geothermal use under various conditions.

1. Configuration I

Configurations IA (Fig. 8) and IB (Fig. 9) have been developed as prototype configurations which are compatible with the addition of the indicators to drilling fluids. The procedure for preparation of configuration IA is given below.

Pans of 3/16" diameter were manufactured from S3-6 Nectic alloy obtained from Perfection Mica Company. The Curie temperature of the alloy is 410°C, and small pans can easily be picked up with a magnet.

The pans were then stamped with an alphanumeric punch set and flattened again to provide a smooth melting surface on the interior bottom. The pan bottoms were painted red for good contrast using Dupli-color, heat-resistant engine enamel. After drying, the pans were swabbed with GE SS4155 blue silicone primer to improve the adhering qualities of the subsequent silicone rubber seal.

Two sets of 44 indicator pans were prepared. Alloys were employed in 42 cases as the indicator material. The alloys were prepared for insertion into

TABLE 1 - LISTING OF CANDIDATE MATERIALS

Temp. marks	Compound Name or Alloy Composition (wt.%)	Melting point (°C)	Melting range (°C)	Melting point change (°C/1000psi)
A	[Bi 48.5, In 41.5, Cd 10	76	<0.1	0.028
B	[Diphenyl carbonate	77	<0.1	
D	[In 52.34, Bi 47.66	88	<0.1	0.023
E	[4-(dimethylamino)-benzophenone	88	0.2	
F	Bi 52.5, Pb 32, Sn 15.5	96	0.3	-0.031
H	Bi 54, Sn 26, Cd 20	103	0.3	0.024
I	[Fluoranthene	109	0.4	
J	[Bi 67, In 33	110	<0.1	-0.079
L	In 52, Sn 48	118	<0.1	0.52
M	[Bi 56.5, Pb 43.5	126	0.4	-0.12
N	[Piperine	128	1.3	
O	Bi 56, Sn 40, Zn 4	133	0.5	0.054
P	[Bi 60, Sn 40	139	0.4	-0.025
R	[2,4-dihydroxyacetophenone	144	0.2	
S	[Bi 60, Cd 40	147	0.5	-0.0067
T	[Thianthrene	155	0.2	
U	Sn 68.35, Cd 29.25, Zn 2.4	159	<0.1	0.77
X	Sn 71, Pb 24, Zn 5	170	0.3	0.39
Y	[1,3,5-triphenylbenzene	174	0.9	
Z	[Sn 67.75, Cd 32.25	175	<0.1	0.084
2	Sn 62.5, Pb 36.15, Ag 1.35	180	0.2	0.26
3	Sn 61.9, Pb 38.1	184	0.6	0.32
5	Sn 91, Zn 9	198	<0.1	0.22
6	Sn 91, Mg 9	205	0.8	0.42
7	6-Nitrobenzimidazole	207	1.7	
A•	2-Phenylquinoline-4-carboxylic acid	214	<0.1	
B•	Sn 95.8, Ag 3.5, Cu 0.7	218	0.7	0.26

D•	Sn 96.5, Ag 3.5	222	0.1	0.26
E•	Sn 99.5, Al 0.5	229	0.7	0.24
F•	Sn	231	0.3	0.29
H•	Sn 99.41, Cu 0.32, Al 0.27	234	0.1	0.26
I•	Pb 79.7, Cd 17.7, Sb 2.6	239	0.4	0.34
J•	Pb 84, Sb 12, Sn 4	243	0.6	0.31
K•	Pb 82.6, Cd 17.4	249	0.1	0.20
L•	Pb 88.9, Sb 11.1	253	<0.1	0.21
M•	Bi 97.3, Zn 2.7	256	0.7	-0.21
N•	Bi 97.5, Ag 2.5	263	0.6	-0.22
O•	Cd 82.6, Zn 17.4	265	0.2	0.34
P•	Bi	273	0.2	-0.26
R•	Pb 91, Sb 4.68, Cd 4.32	276	<0.1	0.36
S•	Ga 82, Mg 18	285	1.5	0.053
T•	Cd 92.45, Sb 7.55	294	0.6	0.50
U•	Pb 96.97, Ag 2.20, Sb 0.83	301	<0.1	0.68
X•	Pb 97.5, Ag 2.5	303	0.4	0.48
Y•	Pb 97.55, Ag 1.75, Sn 0.7	311	<0.1	0.49
Z•	Pb 98.1, Sb 1, Zn 0.9	315	0.5	0.59
2•	Pb 97.4, Sn 2.6	320	0.5	0.61
3•	Pb 98.76, Sn 1.24	325	0.5	0.49
5•	Pb	329	0.5	0.58
6•	Zn 92.97, Al 4.08, Mg 2.95	344	0.3	0.30
7•	Te 70.6, Ag 29.4	351	1.4	0.47

Fig. 8 TEMPERATURE INDICATOR CONFIGURATION IA

Same as the previous configuration
except the pan wall is crimped.

Fig. 9 TEMPERATURE INDICATOR CONFIGURATION IB

the pans in most cases by rolling to a 0.3mm thickness. Several alloys were too brittle to be rolled and were melted instead in flattened glass tubing to approximate as closely as possible a 0.3mm thick sheet. The alloys were then cut and formed into 3/16" by 1/16" bars which were placed in the center of the pans. Clear mica windows of 3/16" diameter were fitted over the alloys in preparation for sealing.

Two of the indicator materials were organic compounds. Small amounts of these in powdered form were placed in the pans and flattened smoothly with mica windows.

The sealing process involved several steps. GE RTV-615A High Strength Silicone Rubber with its curing agent RTV-615B was prepared in a 10 to 1 proportion by weight. This mixture was stirred well and allowed to sit at room temperature for approximately 3 hours to settle and thicken. It was then stored in the freezer in small quantities for future use. Before use, the silicone was allowed to return to room temperature.

Sealing and curing were accomplished on a hot plate set at approximately 65°C. Curing was completed in 1/2 hour.

The first indicator package set was melted by placing the indicator pans on a hot plate slightly hotter than the melting temperature of the sample and pressing to spread the alloy, simulating the down-hole pressure effect anticipated in drilling fluid use.

Typically, a finished alloy indicator package weighs about 80 mg with a volume of 0.037 cm³. Thus the overall density is about 2.2 g/cm³. Effective decreases in density can be achieved, if required, using higher cylinder walls.

2. Configuration II

Configurations IIA (Fig. 10) and IIB (Fig. 11) are designed for use in non-thermal tools, such as a directional survey tool. The configuration illustrated in Fig. 10 has been constructed. The container design shown in Fig. 11 has not yet been constructed but should present no problem. In configuration IIA, the temperature indicator discs, separated by thermally conductive inert spacers, were stacked on top of each other in melting temperature order, and the stack spring-loaded. The whole stack including the spring is threaded on a rod. As an indicator melts, it is squeezed out of the stack in liquid form.

3. Configuration III

This configuration involves the use of alloy temperature indicator materials to calibrate high temperature electronic means of measuring temperature, in situ, i.e. in an actual geothermal well. For example, a simple circuit such as that indicated in Fig. 12 could be used in parallel with the electronics package to be calibrated. Here, when the melting point of temperature indicator (TI₁) is reached, the series resistance of the circuit increases by R₁, similarly with TI₂-R₂ etc. These resistance steps provide temperature markers to calibrate the electronics output.

ALLOY MELTING POINT FROM THE SPRING-LOADED END

<u>°C</u>
88
96
103
110
118
red bead
126
133
139
147
159
red bead
170
175
180
184
198

Fig. 10 CONFIGURATION II A - SPRING LOADED ALLOY STACK

Fig. 11 CONFIGURATION II B

FIG. 12 CONFIGURATION III FOR TEMPERATURE CALIBRATION

E. TESTING OF ALLOYS AND INDICATOR CONFIGURATIONS

1. Thermal Testing

Several tests were run on alloy melting behavior and on the durability of the indicator configuration package.

The first tests were run on the alloys themselves to determine the visibility of the melting process and the reliability of the melting temperature. Several wire loops were strung with disc-shaped alloy separated by glass beads.

The first loop contained alloys A(76°C), D(88°C), F(96°C) and J(110°C). This loop was immersed in water and the temperature was raised slowly to 100°C. A, D and F melted at 78°C, 90°C and 98°C respectively, as indicated by an immersion thermometer. After calibration, the thermometer was shown to be reading 1° high; the remaining 1° difference was attributed to the lag time built into the experiment itself.

Samples of 31 alloys with melting points over a temperature range of 126°-329°C were threaded on a second loop. The loop and thermometer were immersed in a 600 ml. beaker of silicone oil which had been shown to be stable up to 250°C. The temperature was increased at a rate of approximately 0.5°C/min. and the alloys were examined for signs of melting. At 240°, the silicone oil expanded to the point of spilling on the hot plate and the experiment was stopped. Sixteen of the alloys with DSC determined melting points below 240° visibly melted by beading or crumbling within 1 or 2° of the DSC determined temperatures. The 15 alloys with DSC determined melting points above 240° remained intact on the loop.

Next, the red paint and silicone rubber seal of Configuration IA were tested for durability. Four pans were sprayed with red paint and sealed with silicone. They were then hung on wire and immersed in silicone oil. The temperature was raised to 250° and maintained for 30 minutes. Above 215°C, the paint gradually darkened, still providing good background contrast, but did not crack or otherwise break down. The silicone seal remained intact.

Two further tests were conducted on the silicone seal. Two completely prepared pans were heated to 250°C in a muffle furnace and left for one hour. No decomposition was observed after this period of time. One of the pans was then heated to 300°C. After 30 min., no decomposition was evident. The furnace was then equilibrated to 350°C. After 15 minutes, the seal was intact. After 45 minutes, the seal cracked and broke apart under slight pressure. This test in the hot dry oven indicated that the durability of the silicone rubber seal is considerably reduced at temperatures above 300°C. However, such a problem should be easily overcome by simply crimping the indicator pan in the manner of configuration IB discussed previously. Furthermore, a perfect seal should not be absolutely necessary since the candidate materials were selected to be insoluble and non-reactive in geothermal fluids. Indeed, any sealing or crimping, it is believed, will be satisfactory so long as it holds the whole indicator package - pan, candidate compound and mica window - in one piece.

2. Hydrodynamic Testing

To obtain an estimate of how well the indicator configuration might be carried in drilling fluids, the following preliminary experiment was performed. An indicator package with Configuration IA shown in Fig. 8 was dropped in a 42" water column simultaneously with some rock cuttings obtained from the LASL hot dry-rock well at Valles Caldera. They all fell at almost the same steady velocity and hit the bottom in 8-9 seconds. When another indicator package with a density purposely made double to the first was tested, transit time in the same water column was about halved, 4-5 seconds. This experiment implies that the IA configurations can be carried in the drilling fluid with about the same ease as rock cuttings.

3. Corrosion Testing

The corrosion resistance of the "Nectic" pan material was tested. The material withstands boiling for an hour in an aqueous 5 percent sodium carbonate solution, containing 5 percent sodium chloride with no sign of corrosion. It also withstands 5 percent sodium chloride containing 5 percent acetic acid. It was attacked only very slowly with concentrated hydrochloric acid.

4. Stress Resistance Testing

Some preliminary experiments were carried out to test the stress resistance of simulated indicator configurations. Note that these tests were performed using 1/4" Aluminum DSC sample pans before the "Netic" pans were available. The tests were performed in a laboratory ball mill containing a liquid suspension of the following composition to simulate drilling fluid:

water	500 ml
bentonite	25 g
fine sand	50 g
coarse sand (3/16")	50 g
sodium carbonate	1.0 g

Tests were performed on the following configurations:

1. DSC sample pans with mica windows crimped and sealed with silicone
2. DSC sample pans with mica windows uncrimped and filled with silicone

Samples of the above configurations were placed in the ball mill containing the simulated drilling fluid and milled for 1 hour. Both configurations came through the ball milling apparently unscathed. The samples were weighed before and after testing and no change in weight was noted.

IV COST ANALYSIS

All indicator materials and configurations to date have been "hand made" in the laboratory. It is of critical interest to estimate the cost of temperature indicators in production quantities, so that a cost/benefit analysis can be carried out vis a vis competitive techniques. The analysis refers to a complete series of 44 indicator materials in a configuration compatible with addition to drilling fluid (Configuration IA or IB discussed above). Costs presented below are for 1000 indicators, i.e. 22.7 complete series of 44 indicator materials.

A. RAW MATERIALS

Alloys and Organics	\$50	
Oxygen	10	
Glass Tubing	3	
Nitrogen	7	
Mica	15	
Netic Sheet	15	
Recorder Paper	7	
Total Materials		\$107

B. CONFIGURATION FORMATION

Die Setting	\$ 45	
Formation of Pans	250	
Production of Mica Windows	70	
Sub Total		\$365
Total A + B		\$472

C. OTHER COSTS

The configuration formation costs noted in B above are firm, since these items are provided by a vendor at the indicated prices. The largest additional costs are labor involving cutting out alloy bars, putting together the final indicator configuration and sealing. Undoubtedly, in production, special jigs, etc. will facilitate these tasks and allow them to be performed by relatively unskilled labor. It is estimated that additional labor costs and associated overhead will be \$528 or less. Thus the cost of each indicator is estimated at \$1 or less.

D. COMPARISON WITH PRESENT METHODS

The principal cost element in the electronic techniques for temperature measurement is drilling rig time for a temperature measurement trip. The cost involves such factors as depth of hole, size of rig, etc. Typically, a temperature measurement costs at least \$1,000 with present techniques.

The use of the chemical temperature indicators appears to represent a cost saving of at least an order of magnitude over present techniques. If the temperature of interest were known within 40°C, for example, as 200°C $\pm$ 20°C

the use of 7 different indicators, 2 through B. in Table 1, page 14 would be involved. Assuming conservative recovery statistics, that 10 duplicates of each indicator must be used to insure that at least 1 of each will be recovered, total indicator costs are \$70 or less (Telephone discussions with Mobil Research and Development personnel have confirmed that this recovery estimate is conservative, if the drill bit is lifted off hole bottom during the time of passage of the indicators through the orifices in the bit.).

V. CONCLUSIONS

1. The use of solid to liquid first order phase transitions to measure temperatures in geothermal wells during the drilling process is feasible.

2. A series of 51 materials with sharp, well-defined melting points has been developed over the temperature range $80^{\circ}\text{C} \leq T \leq 350^{\circ}\text{C}$. Of these, 42 are metals or alloys and 9 are organic compounds. Since 7 of the organics have melting points near corresponding alloys the useful series is comprised of 44 materials.

3. Measurements have been made of the normal melting point, the broadness of the melting range and the heat of fusion for the temperature indicator materials.

4. Temperatures below 170°C are well covered, with temperature intervals being about 10°C , as originally desired. For temperatures above 170°C , there are two major temperature gaps: one between 329°C and 344°C (15°C interval), and the other 184°C to 198°C (14°C interval). The particular importance of these two temperature ranges in geothermal applications will await determination by field experimentation. Except for the two temperature bands noted above, the coverage over the remainder of the temperature range appears to be reasonably good.

5. The effect of pressure on melting temperature is relatively small. Estimates have been made for the metals and alloys with typical results on the order of a few tenths of a $^{\circ}\text{C}$ per 1000 psi. True values should be experimentally determined.

6. Indicator configurations have been developed to allow use of the materials in circulating drilling muds. Recovery of the indicators can be effected at or near the shale shaker.

7. Indicator configurations have been developed for use in non-thermal sondes and tools.

8. The temperature indicators can be useful for in-situ calibration of high temperature electronic techniques for measuring temperature.

9. Temperature indicators can be made in production quantities for \$1 each or less. This represents at least an order of magnitude cost saving over competing electronic techniques.

VI RECOMMENDATIONS

A program for further development of the temperature indicators, emphasizing actual field testing, has been discussed in detail elsewhere (11). Only a brief summary will be presented below.

1. The indicator configurations should be tested at elevated pressures ($P \leq 7000$ psi) and various temperatures in a typical drilling fluid composition using a laboratory test loop of another government contractor. The test results are of interest not only to measure the effect of pressure on melting temperatures, but principally to allow improved configuration design and construction, as required.

2. The temperature indicators should be field tested in non-thermal sondes and tools, such as a directional survey tool.

3. Field tests should be run in which the indicators are left on hole bottom during a trip and subsequently carried to the surface in the drilling fluid.

4. Field tests should be run in which the indicators are added to circulating drilling fluid, carried down the drill string through the orifices in the drill bit and returned to the surface in the drilling fluid. Such tests will allow development of reliable indicator recovery statistics and recovery techniques.

5. The temperature indicators should be field tested for in situ calibration of electronic methods of temperature measurement.

6. Field testing should be performed in a variety of geothermal environments, i.e. hot concentrated brine, dry steam, hot dry rock and geopressured geothermal.

7. If field tests of the temperature indicators are successful, attention should be directed toward the development of time-temperature integrator materials and techniques for improved temperature-depth profiles.

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