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(54) **Metal quenchants.**

(57) Novel metal quenchants, which are particularly suitable for quenching steels, are provided. The quenchants comprises an aqueous solution to a polyoxyalkylene glycol and an oxazoline polymer. Such quenchants are more oil-like in their behaviour than the aqueous polyoxyalkylene glycol quenchants of the prior art and hence are less likely to introduce stresses into metals such as steel when they are quenched.

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METAL QUENCHANTS

The present invention relates to metal quenchants which are used in the heat treatment of metals. In particular, the present invention relates to novel metal quenchants containing oxazoline polymers and to heat treatment processes which employ such metal quenchants.

It is well known that the physical properties of metals and alloys can be modified or improved by heat treatment and various heat treatments have been devised which allow such modifications or improvements to be carried out. Typically such treatments involve heating the metal to an elevated temperature below its melting point and subsequently cooling it to room temperature. The cooling process, usually called "quenching", is accomplished by immersing the hot metal in a bath of a liquid, such as water or oil, which has a large thermal capacity and can absorb the heat of the metal.

For many quenching applications, for example in cooling hot alloy steels, water is however not suitable. This is because water cools the metal so rapidly that stresses are introduced which tend to cause cracks or deformations to appear in the cold metal. In steel this is a particular problem since, on rapid cooling not only do thermal stresses appear but, for steels heated above their austenitisation temperature, there appear also transformation stresses.

Transformation stresses in steels arise because during quenching, the steel transforms from a high temperature stable Austenite phase having one structure to a low temperature stable

Martensite phase having a different physical structure. Since the Austenite phase is denser than the Martensite phase the overall effect of the transformation is to cause the metal to expand. If however the steel is quenched too rapidly, transformation of
5 Austenite to Martensite occurs initially at the metal surface only, resulting in a steel having regimes of the Martensite phase surrounding the Austenite phase. Subsequent transformation of the residual Austenite phase then generates surface tensile stresses in the cold steel thereby increasing the likelihood that the steel will
10 crack or deform.

In such situations, oil can be used as an alternative to water. However although oil quenches metal at a slower rate than water does, it suffers from the disadvantages of (1) being flammable and (2) of being prone to foul the metal surface. It is desirable,
15 therefore, to produce a quenchant having quenchant properties similar to those of oil without the associated drawbacks.

US 4,486,246, discloses an aqueous based metal quenchant fluid which has properties more comparable with oil than water while avoiding flammability and fouling problems. The quenchant comprises
20 an aqueous solution of a non-ionic water-soluble or water-dispersable substituted oxazoline polymer having recurring units of the formula $-[N(COR)CH_2CH_2]-$ where R is an organic radical. The quenchants are claimed to be of lower viscosity than, for example, aqueous polyoxyalkylene quenchants such as are
25 described in US 3,220,893.

It has now been discovered that improved cooling rates over those obtained using quenchants of the type disclosed in US 4,486,246 and the prior art can be obtained using aqueous polyoxyalkylene quenchants containing oxazoline polymers.

30 Accordingly, the present invention provides a quenchant for use in the heat treatment of metals or alloys characterised in that the quenchant comprises an aqueous solution of a polyoxyalkylene glycol and a oxazoline polymer.

As regards the polyoxyalkylene glycol this is suitably a
35 poly(oxyethylene)(oxypropylene) glycol, known in the art as a PAG,

made by polymerising ethylene oxide and propylene oxide on an alcohol or polyfunctional alcohol starter. The poly(oxyethylene)(oxypropylene) glycol can be either a random or block copolymer. In addition the polyoxyalkylene glycol should preferably have a viscosity in the range 15-30,000 centistokes at 40°C (corresponding to a molecular weight in the range 10,000-20,000). The polyoxyalkylene glycol suitably constitutes between 2 and 25% by weight of the quenchant preferably between 5 and 20%.

The oxazoline polymers which can be used in the quenchants of the present invention have been disclosed in US 4,486,246. These oxazoline polymers are water soluble or water dispersable and are suitably constructed of units having the formula

$-[N(COR)CH_2CH_2]-$ where R is an organic group selected from the group consisting of substituted or unsaturated phenyl groups and C₁-C₇ alkyl groups. It is preferable that the oxazoline polymer has a molecular weight in the range 5000-1,000,000 most preferably 50,000-750,000 and that at least 50% of the R groups are a C₁-C₃ alkyl groups. Preferred R groups include methyl, ethyl, propyl, butyl, isobutyl, phenyl and substituted, e.g. halogenated and alkoxyated, derivatives thereof. The oxazoline polymer may be either a homopolymer or a copolymer made from one or more types of the units mentioned.

Oxazoline polymers can be prepared by polymerising unsaturated oxazoline monomers under an inert atmosphere in the presence of a catalyst. A method which may be used to carry out a polymerisation is described in US 3,483,141. Certain oxazoline polymers, e.g. polyethyloxazoline, are commercially available.

The oxazoline polymer should be present in the quenchant in amounts corresponding to between 0.1 and 5% by weight of the quenchant. Preferably between 0.5 and 2% by weight oxazoline polymer should be used.

In general the rate of quenching decreases as the concentration of the oxazoline polymer in the quenchant increases. Likewise the rate of quenching decreases as the concentration of polyoxyalkylene

glycol in the quenchant increases. The presence of large quantities of polyoxyalkylene glycol should be avoided if possible, however, in order to avoid the quenchant becoming too viscous.

In addition to the components described above other components, familiar to those skilled in the art, may optionally be added to improve the performance of the quenchant. Such components include corrosion inhibitors, for example sodium nitrite and alkanolamines, defoamers, biocides and metal deactivators.

As mentioned previously, although they can be used with any metal or alloy the quenchants of the present invention are particularly suitable for the quenching of steels and especially so far those which have been heated above their Austenite-Martensite transition temperature. The exact temperature of this transition will depend upon the exact composition of the steel. Typically the quenching is carried out by immersing an ingot or casting of the hot steel in a large bath or vat of the quenchant. Once the steel is cool, it is removed and washed to remove any quenchant adhering to it.

The quenchants of the present invention may be supplied to those who use it as an aqueous solution. However it may also be supplied in the form of a concentrate comprising the polyoxyalkylene glycol and the oxazoline polymer which is suitable for dilution with water immediately prior to use. Suitably, such concentrates have polyoxyalkylene glycol to oxazoline polymer weight ratios in the range 1:2.5-250:1 preferably 2.5:1-40:1.

The invention described above is illustrated by reference to the following examples.

Example 1

A sample of a quenchant comprising 1% PEOX (polyethyloxazoline; $R=C_2H_5$ having a molecular weight of 500,000) plus 16% of a polyoxyalkylene glycol (comprising a diol started 75:25 ethylene oxide/propylene oxide copolymer glycol (53%) in water) was placed in a 2600 ml beaker. The contents of the beaker were agitated by a propeller stirrer in conjunction with an H-baffle. The bath temperature was 25°C.

A probe, manufactured of Inconel 600 (Inconel is a registered trade mark), which was 60mm long and 12.5mm in diameter was heated to 850°C and soaked at temperature for 5 minutes. The temperature of the probe was measured by means of an NiCr/NiAl thermocouple mounted at the geometric centre of the probe.

On completion of the 850°C soak the probe was mechanically plunged into the quench in an operation which took less than 3 seconds. A desk top computer, activated by the plunging operation then recorded the temperature of the probe as a function of time.

The data obtained are shown in Figures 1 and 2 expressed as time-temperature and temperature-temperature differential plots.

Comparative Test A

The method used in Example 1 was followed except that water was used in place of the polyoxyalkylene glycol in the quenchant.

Time-temperature and temperature-temperature differential plots are also shown in Figure 1.

Comparison of the data from Example 1 and Comparative Test A shows that the quenchants of the present invention cool the probe more slowly than the quenchants of the prior art (US 4,486,246) and hence are more oil-like in their behaviour.

Example 2

The method of Example 1 was repeated except that 2% by weight PEOX was used. The time-temperature and temperature-temperature differential plots are shown in Figures 3 and 4 respectively.

Comparative Test B

Example was repeated except that the PEOX was omitted from the quenchant. The time-temperature and temperature-temperature differential plots are shown in Figures 3 and 4 respectively.

Comparative Test C

Example 1 was repeated except that a sample of a cold quenching oil after a period of industrial service was used as quenchant. The time-temperature and temperature-temperature differential plots are shown in Figures 3 and 4 respectively.

Figures 3 and 4 show that the quenchants of the present invention are more oil-like in their behaviour than the

polyoxyalkylene glycol/water or the oil quenchants of the prior art. Hence the quenchants of the better invention will be better for cooling steels and the like.

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Claims:

1. A quenchant for use in the heat treatment of metals or alloys characterised in that the quenchant comprises an aqueous solution of a polyoxyalkylene glycol and an oxazoline polymer.
2. A quenchant as claimed in Claim 1 wherein the oxazoline
5 polymer has a molecular weight in the range 50,000 to 750,000.
3. A quenchant as claimed in either Claim 1 or Claim 2 wherein the oxazoline polymer comprises units having the formula -
[N(COR)CH₂CH₂] - wherein at least 50% of the R groups are C₁
to C₃ alkyl groups.
- 10 4. A quenchant as claimed in Claim 3 wherein the oxazoline polymer is polyethyloxazoline.
5. A quenchant as claimed in any one of the preceeding Claims comprising an aqueous solution of between 5 and 20% by weight polyalkylene glycol and between 0.5 and 2% by weight oxazoline
15 polymer.
6. A process for quenching a metal or an alloy which process comprises immersing an ingot or casting of the hot metal or alloy in a bath of quenchant as defined in Claim 1.
7. A process as claimed in Claim 6 wherein the metal or alloy
20 used is steel.
8. A process as claimed in either Claim 6 or Claim 7 wherein the quenchant comprises an aqueous solution of a polyoxyalkylene glycol and polyethyloxazoline.
9. A metal quenchant concentrate which when diluted with water
25 forms a quenchant as defined in Claim 1 wherein the metal quenchant

concentrate comprises a mixture of a polyoxyalkylene glycol and a oxazoline polymer.

10. A metal quenchant concentrate as claimed in claim 9 wherein the polyoxyalkylene glycol to oxazoline polymer weight ratio is in the range 2.5:1-40:1.

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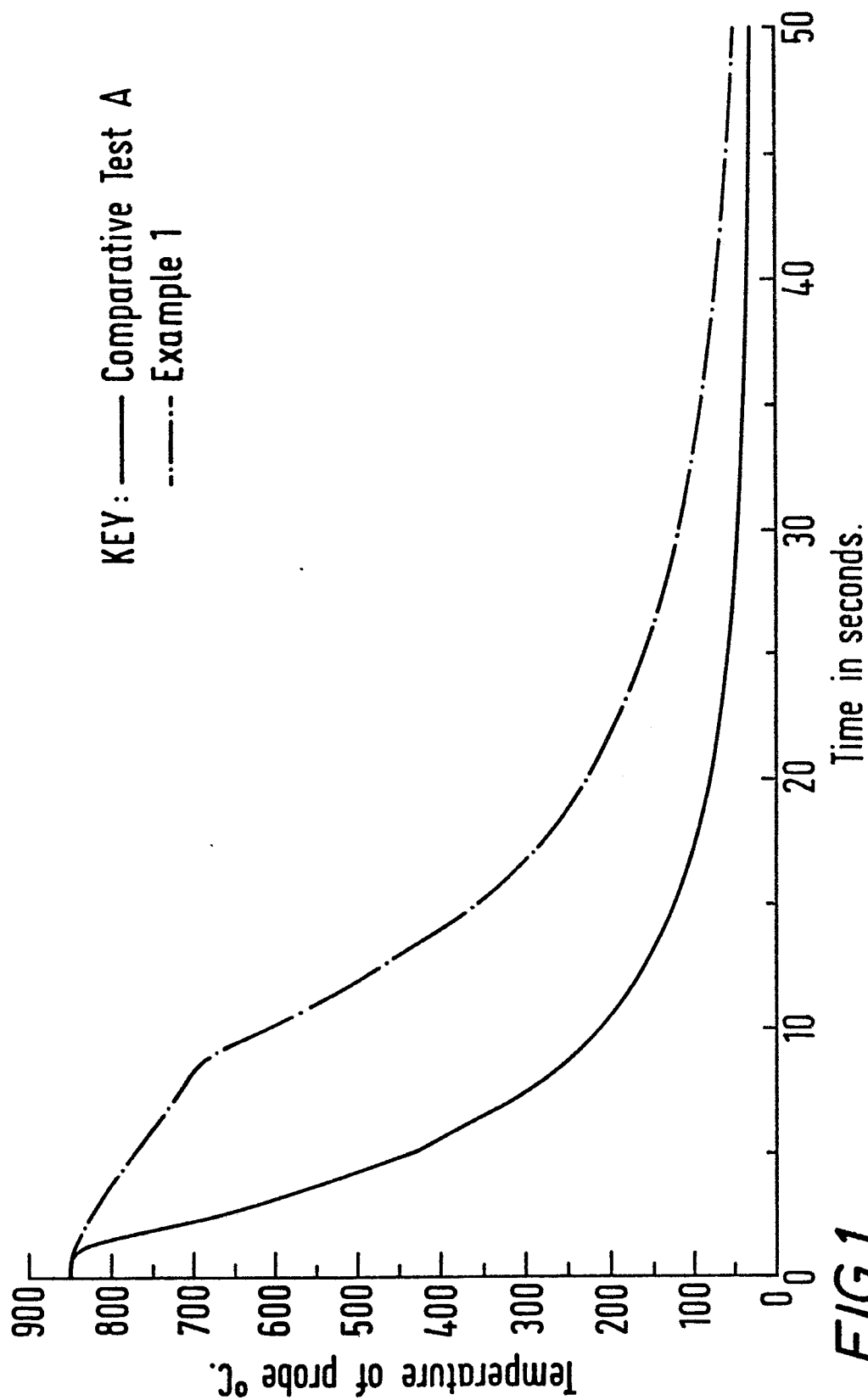
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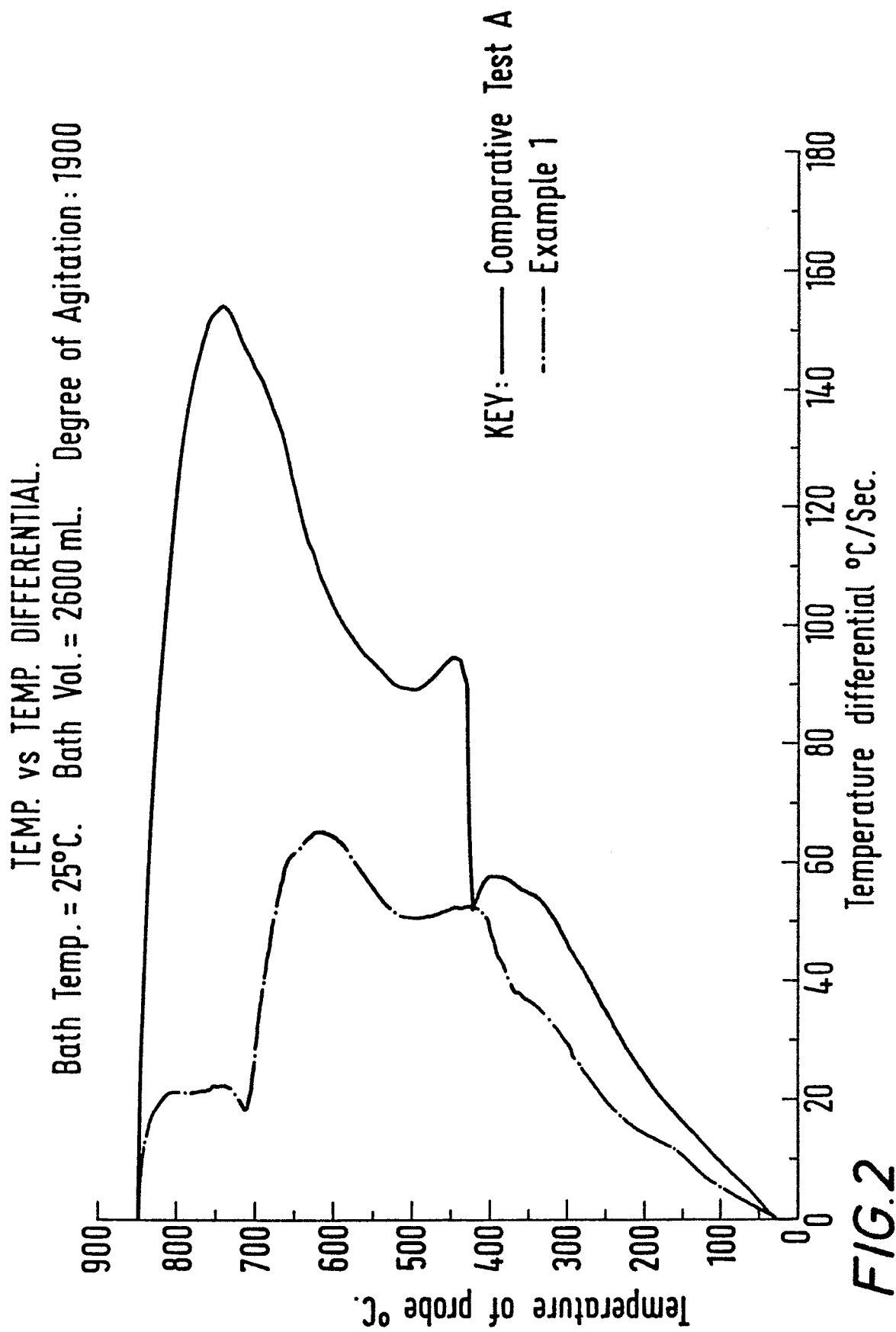
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TEMPERATURE vs TIME CURVE.
Bath Temp. = 25°C. Bath Vol. = 2600 mL. Degree of Agitation : 1900





TEMPERATURE vs TIME CURVE.
Bath Temp. = 25°C. Bath Vol. = 2600 mL. Degree of Agitation : 1900

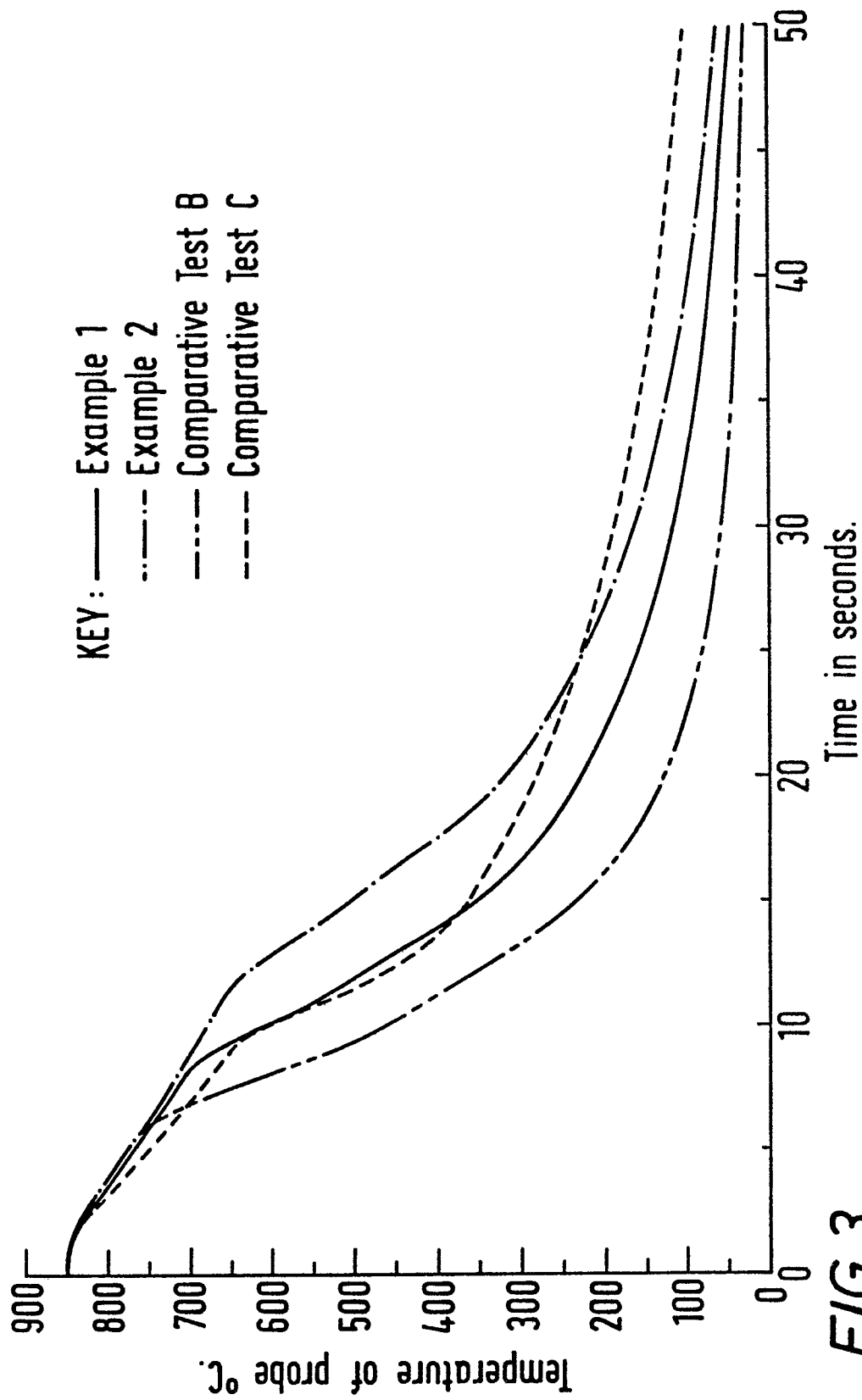
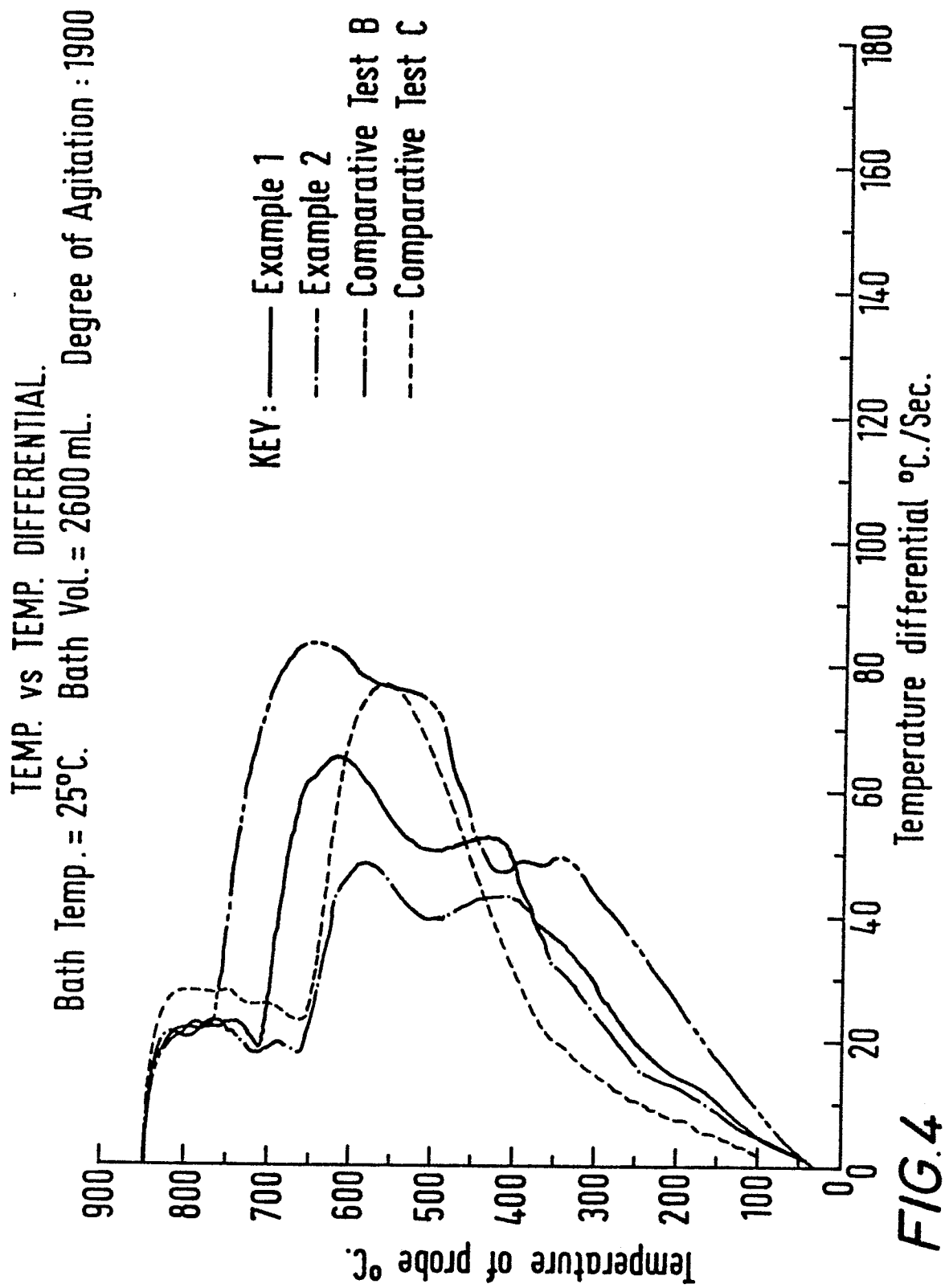


FIG.3





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
A,D	US-A-3 220 893 (BLACKWOOD et al.)		C 21 D 1/60

A,D	US-A-4 486 246 (WARCHOL)		

A,D	US-A-3 483 141 (LITT et al.)		

			TECHNICAL FIELDS SEARCHED (Int. Cl. 4)
			C 21 D 1/60
The present search report has been drawn up for all claims			
Place of search BERLIN		Date of completion of the search 23-05-1986	Examiner SUTOR W
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	