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Quenching fluid and its use for quenching metallic articles.

The quenching fluid comprises i) water and ii) a copolymer containing, in polymerized form, an α,β -ethylenically unsaturated carboxylic acid, an ethylenically unsaturated amide and a hydrophobic monomer having limited solubility in water. The maximum cooling rate of the quenching fluid is not considerably higher than the maximum cooling rate of a mineral oil.

The present invention relates to a quenching fluid and its use for quenching or cooling metallic articles.

It is well known that optimal mechanical properties of metallic articles, such as iron alloys or steel, for example carbon steel or alloyed steel, are only achieved when the metallic article is heated to an increased temperature and then quenched. The conditions of quenching or cooling the metallic article, such as the quenching rate, have a great influence on the mechanical properties of the metallic article. Using a proper quenching rate is essential in order to obtain the desired properties of the metallic article after cooling. If suitable quenching conditions are not employed, deformations or even cracking during hardening of the metallic article may occur. Cooling which is too fast may result in an article containing a hardened surface and a soft center because the surface cools more rapidly than the center.

Methods of quenching or cooling metallic articles are generally known. Quenching of the hot metallic article is generally done in a liquid or free-flowing medium. Depending on the desired cooling rate, an aqueous or oily quenching fluid or a molten salt is utilized. Theory and practice of quenching steels are discussed, for example, in "Metals Handbook", 8th edition, edited by the American Society of Metals, in volume 2 in the chapter "Quenching of Steel", pages 15-36.

When an aqueous quenching agent is utilized, the cooling of metallic articles, such as steel, occurs in three stages, each of which has different characteristics. In stage 1, commonly called vapor blanked stage, a vapor film surrounds the metallic article. Heat is removed from the article by the formation of the vapor layer. Heat transfer is by radiation and conduction through the vapor film. Stage 1 usually is a period of slow cooling. Stage 2 is generally called vapor transport or boiling stage. In stage 2 the quenching fluid in contact with the surface of the metallic article boils and disperses the film of vapor. Bubbles of vapor are formed. In stage 2 the cooling rate usually reaches a maximum. In stage 3, the liquid cooling stage, boiling of the quenchant ceases and heat is removed by convection. Stage 3 usually is a period of slow cooling.

In order to modify the quenching conditions in water, such as its maximum quenching rate, various additives have been utilized.

U.S. Patent 3,996,076 discloses a quenching medium for metals which essentially consists of an aqueous solution containing 0.4 to 10 weight percent of polyacrylic acid, polymethacrylic acid or a copolymer of acrylic and methacrylic acid.

WO 83/03566 suggests as the quenching medium for quenching metals an aqueous solution which contains 0.5 to 50 percent by weight of a liquid, water-soluble, capped polyether polyol obtained by reacting ethylene oxide and at least one lower alkylene oxide having 3 or 4 carbon atoms with an active hydrogen compound, such as a lower glycol, and further reacting the copolymer with an alpha olefin oxide.

U.S. Patent 5,141,662 discloses heat transfer fluids which are used as solder fluids and in metal quenching and tempering baths. The heat transfer fluid contains a polyether polyol produced by reacting one or more low molecular weight alkylene oxides with one or more saccarides. The reaction products typically have molecular weights in the range of 700 to 1800.

Further, various polyoxyalkylene glycols have been suggested for modifying the quenching conditions of water. German Offenlegungsschrift DE-A-32 20 931 discloses an aqueous quenching medium containing 0.1 to 30 weight percent of a polyoxyalkylene glycol ether of a molecular weight of 4,000 to 30,000 and 0.5 to 15 weight percent of a corrosion inhibitor.

Besides many advantages, such as lack of fire hazards and fuming, polyoxyalkylene glycol/water-based quenchants have some disadvantages, such as a cloud point of about 65°C which limits the maximum working temperature of the quenchant. Furthermore, the cooling rate of polyoxyalkylene glycol/water based quenchants is relatively high and, accordingly, not useful for cooling steels having a high carbon content or other metallic articles that require a low cooling rate.

Quenchants based on mineral oils are commonly used in applications where a low cooling rate is desired. Unfortunately, a high fire risk is involved in the use of mineral oils for quenching metallic articles.

U.S. Patents 4,087,290 and 3,939,016 suggest mixtures of a salt of polyacrylic acid and water as a quenchant. However, at about 300°C where a low cooling rate is essential, the cooling rate of polyacrylate/water-based quenchants is generally higher than the cooling rate of mineral oil. Furthermore, polyacrylates lead to different cooling curves when the temperature of the cooling bath fluctuates substantially.

One aspect of the present invention is a quenching or cooling fluid which comprises

i. water; and

ii. a copolymer containing, in polymerized form, an α,β -ethylenically unsaturated carboxylic acid, an ethylenically unsaturated amide and a hydrophobic monomer.

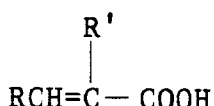
Another aspect of the present invention is a method of quenching or cooling a metallic article by contacting the article with the quenching fluid of the present invention.

At least in its preferred embodiments, the invention is able to provide a new water-based quenching fluid which has a cooling rate at 300°C which is not substantially higher than the cooling rate of a mineral oil at 300°C.

The quenching fluid of the present invention preferably comprises from 0.1 to 40, more preferably from 1 to 30 and most preferably from 2 to 20 percent of a copolymer described below and preferably from 60 to 99.9, more preferably from 70 to 99 and most preferably from 80 to 98 percent water, based on the total weight of the copolymer and water.

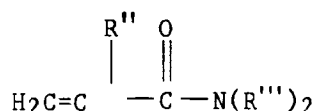
The copolymer contains, in polymerized form, an α,β -ethylenically unsaturated carboxylic acid, an ethylenically unsaturated amide and a hydrophobic monomer. Such copolymers and methods of preparing them are described in U.S. Patent 4,423,118.

Of the monomers employed, the α,β -ethylenically unsaturated carboxylic acid advantageously contains from 3 to 8 carbon atoms. Preferred carboxylic acids are generally represented by the formula



wherein R is -H, -COOX or -CH₃ and R' is H, an alkyl group having from 1 to 4 carbon atoms or -CH₂COOX wherein X is -H or an alkyl group having from 1 to 4 carbon atoms. Preferably, R is -H or -CH₃ and R' is H or an alkyl group having from 1 to 4 carbon atoms. More preferably, the unsaturated acid is acrylic or methacrylic acid with acrylic being most preferred. In general, other acids such as itaconic, fumaric, crotonic or aconitic acid and the half esters of a polycarboxylic acid such as maleic acid with C₁-C₄ alkanols are employed only in combination with acrylic or methacrylic acid.

The ethylenically unsaturated carboxamide is advantageously represented by the following formula:



wherein R'' is H or an alkyl group of 1 to 4 carbon atoms and each R''' is individually -H, an alkyl group of 1 to 4 carbon atoms or a hydroxyalkyl group of 1 to 4 carbon atoms provided that at least one R''' is -H. More preferably, the unsaturated carboxamide is methacrylamide or acrylamide, with acrylamide being most preferred.

The hydrophobic monomer employed in preparing the copolymer is an ethylenically unsaturated monomer which generally has a limited solubility or miscibility in water. By "limited solubility" is meant that the monomer generally forms a 1 to 10 weight percent solution in water at a temperature of about 40°C, without the aid of a solubilizing agent. Generally the monomer, when homopolymerized, forms a water-insoluble or water-immiscible polymer, that is, a polymer that forms less than a 1 weight percent aqueous solution at about 40°C. Representative of such hydrophobic monomers are acrylonitrile, methyl acrylate, methyl methacrylate or vinyl acetate.

The copolymer contains, in copolymerized form, from 30 to 97, preferably from 35 to 85, most preferably from 40 to 60 percent of the α,β -ethylenically unsaturated carboxylic acid, from 1 to 50, preferably from 5 to 40, most preferably from 15 to 35 percent of the ethylenically unsaturated amide and from 2 to 69, preferably from 10 to 50 and most preferably from 15 to 35 percent of the hydrophobic monomer, by the total weight of the carboxylic acid, the amide and the hydrophobic monomer. Particularly useful copolymers in the quenching fluid of the present invention contain, in copolymerized form, from 45 to 55 percent of the carboxylic acid, such as acrylic acid, from 20 to 30 percent of the amide, such as acrylamide, and from 20 to 30 percent of the hydrophobic polymer, such as acrylonitrile. Although the copolymer may contain minor amounts, that is, less than about 10 weight percent of other copolymerizable monomers, such other monomers are not preferably employed in the preparation of the copolymer, that is, the described copolymer preferably is a terpolymer.

The molecular weight of the copolymer is not particularly critical to the practice of the present invention. In general, the polymer preferably has a molecular weight such that the viscosity of the polymer, as a 16 weight percent solution in water, is from 500 to 15,000 cps, more preferably from 1000 to 10,000 cps, most preferably from 2,000 to 6,000 cps, when said viscosities are measured using a Brookfield viscosimeter, Model LVT, Spindle No. 5 at 20 rpm and 25°C.

The copolymer can be produced in a known way, for example by solution polymerization techniques in the presence of a free radical initiation means, as described in column 5, lines 1 to 52 and Examples 1 and 2 of U.S. Patent 4,423,118.

The quenching fluid of the present invention may contain other components, such as alkali metal halides, for example, sodium chloride, basic compounds, for example, NaOH or KOH, defoamers, emulsifiers, corrosion inhibitors, for example, sodium nitrite, ethanol amine or amine soaps, biocides and metal deactivators.

If such optional additives are contained in the quenching fluid, their amount generally is from 0.1 to 20, preferably from 0.5 to 10 percent, by the total weight of the quenching fluid.

The quenching fluid of the present invention is not based on mineral oil. This means that the total weight of a mineral oil generally is less than 10 percent, preferably less than 5 percent, more preferably less than 2 weight percent, based on the total weight of the quenching fluid. Most preferably, the quenching fluid does not contain an oil.

The quenching fluid of the present invention comprises the above-described copolymer and water. Advantageously, water is the main component of the quenching fluid. Preferably, the quenching fluid comprises from 60 to 99.9, more preferably from 70 to 99 and most preferably from 80 to 98 percent water, based on the total weight of the copolymer and water. A portion of water which is present in the quenching fluid of the present invention may be replaced by one or more water-miscible liquids, such as amine, alcohol or polyalcohol initiated polyalkylene glycols, for example, polypropylene glycols, monoethylene glycol, diethylene glycol or monopropylene glycol; esters, carboxylic acids; long chain alcohols, amines or amides. The quenching fluid generally contains up to 69 percent, preferably up to 40 percent, more preferably up to 20 percent of the water-miscible liquid, by the total weight of the quenching fluid, if a water-miscible liquid is present in the quenching fluid at all.

Although the quenching fluid of the present invention is not based on mineral oils or other oils, it surprisingly has a maximum cooling rate or a cooling rate at 300°C respectively which is not substantially higher than the maximum cooling rate or the cooling rate at 300°C respectively of mineral oil. In many cases it has about the same or even a lower cooling rate than mineral oil. The cooling rate at 300°C of the quenching fluid of the present invention generally is up to 15°C/sec, in many cases only up to 10°C/sec, measured according to the Wolfson test method, utilizing equipment commercially available from Drayton Probe Systems Ltd., England, under the tradename "Quenchmaster." For comparative purposes, the cooling rate at 300°C of a standard mineral oil is up to about 20°C/sec, measured according to the same method. A low cooling rate at about 300°C is essential for many metals because their physical state changes at about 300°C. It is known that the usage of oil-based quenching fluids involves a fire hazard. Fire hazards can be avoided when using the quenching fluid of the present invention.

The maximum cooling rate of undiluted water is about 210°C/sec, measured according to the above-indicated Wolfson test method. Surprisingly, the addition of the above-described copolymer at an amount as low as 2 to 20 percent, by the total weight of water and copolymer, drastically decreases the maximum cooling or quenching rate of the resulting quenching fluid. Furthermore, the maximum cooling rate as well as the cooling rate at 300°C of a quenching fluid of the present invention generally is considerably lower than the maximum cooling rate or the cooling rate at 300°C respectively of known polacrylate/water-based quenchants, as will be illustrated by the examples further below.

In contrast to blends of a polyoxyalkylene glycol and water, no cloud point has been observed when the temperature of the quenching fluid of the present invention rises during the quenching process. Accordingly, the copolymer and water in the quenching fluid generally do not separate at increased temperatures which renders the quenching fluid of the present invention very useful for quenching hot metallic articles.

If for some applications higher cooling rates are desired than obtained with a mixture of water and a copolymer of α,β -ethylenically unsaturated carboxylic acid, ethylenically unsaturated amide and hydrophobic monomer as described above, quenching agents of higher cooling rates may additionally be incorporated into the quenching fluid of the present invention. Such quenching agents are for example polyalkylene glycols disclosed in German Offenlegungsschrift DE-A-32 20 931, polyacrylates as disclosed in U.S. Patents 4,087,290 and 3,939,016 or, preferably, a polyether polyol described below.

A useful polyether polyol is a reaction product of one or more C_{2-4} -alkylene oxides and a polyhydroxy compound containing at least 4 hydroxy groups and at least 5 carbon atoms. Preferred C_{2-4} -alkylene oxides are 1,2- or 2,3-butylene oxide or, preferably, ethylene oxide or propylene oxide. The alkylene oxides may be used individually, alternately in sequence, or in mixtures for reacting with the polyhydroxy compound.

The polyhydroxy compound contains at least 4, preferably from 4 to 16, more preferably from 5 to 8, hydroxy groups and at least 5, preferably from 5 to 24, more preferably from 6 to 12, carbon atoms. The polyhydroxy compound preferably is an aliphatic, more preferably an aliphatic saturated compound. Preferably, 5 or more carbon atoms in the polyhydroxy compound are linked via a chemical bond without an intermediate functional group. For example, 5 or more carbon atoms can form an open-chain or some or all of these carbon atoms may be links of a ring.

The polyhydroxy compound preferably contains at least 5, more preferably from 5 to 21, most preferably from 6 to 11, oxygen-containing groups of which at least 4 groups are hydroxy groups.

5 Preferably all oxygen-containing groups are hydroxy groups, that is, the polyhydroxy compound preferably contains at least 5, more preferably 5 or 6, most preferably 6, hydroxy groups. Exemplary of open-chain polyhydroxy compounds are pentites, such as lyxosite, xylite, arabinite or ribite, or hexites, such as sorbitol or mannitol. Exemplary of cyclic polyhydroxy compounds are cyclites having the formula $6_6\text{H}_{12}\text{O}_6$, such as inosite.

10 Alternatively, the polyhydroxy compound may contain at least 4, preferably from 4 to 14, more preferably from 5 to 8, hydroxy groups and one or more, preferably from 1 to 11, more preferably from 1 to 7, most preferably from 1 to 3 oxygen-containing groups other than hydroxy. Such oxygen-containing groups are for example carboxyl groups, ester groups, such as the methyl or ethyl ester groups, amide groups, preferably tertiary amide groups, or epoxy groups. Preferred oxygen-containing groups are carbonyl groups, such as ketone or aldehyde groups, or ether groups, such as methyl or ethyl ether groups. An oxygen atom may be linked to 4 or more, preferably to 4 or 5, of the above-mentioned carbon atoms to form a cyclic ether. Preferred polyhydroxy compounds are polyhydroxyaldehydes or polyhydroxyketones containing at least 4, preferably from 15 5 to 8 hydroxy groups, and carbohydrates, such as trisaccharides or tetrasaccharides, more preferably monosaccharides or disaccharides. Preferred monosaccharides are ketopentoses, such as ribulose or xylulose; or aldopentoses, such as lyxose, xylose, arabinose or ribose; or aldohexoses, such as allose, altrose, mannose, glucose, idose, talose or galactose; or ketohexoses, such as psicose, sorbose, tagatose or fructose. The D-form of the monosaccharides are generally preferred. Preferred disaccharides are maltose, cellobiose, lactose or saccharose. The (+)-forms of the disaccharides are generally preferred. Sugar derivatives, for example aminosugars such as glucosamines may also be used as a polyhydroxy compound.

20 Besides hydroxy groups and the above-mentioned oxygen-containing groups, the polyhydroxy compound may contain additional functional groups, although the presence of such additional functional groups is not preferred. Preferably, such additional functional groups do not react with an alkylene oxide under the conditions chosen for preparing a polyether polyol. Preferred additional groups are tertiary amide or tertiary amino groups.

The molar ratio between the C_{2-4} -alkylene oxide(s) and the polyhydroxy compound preferably is from 4:1 to 30:1, more preferably from 5:1 to 15:1, most preferably from 6:1 to 9:1.

30 Processes for reacting one or more C_{2-4} -alkylene oxides and an above-described polyhydroxy compound as well as the produced polyether polyol are well known in the art. The weight average molecular weight of the polyether polyol preferably is from 300 to 2500, more preferably from 400 to 2000, most preferably from 500 to 1500. The polyether polyol is biodegradable and is generally miscible with water at any weight ratio at temperatures up to the boiling point of water.

35 If the quenching fluid of the present invention contains an above-described polyether polyol or another quenching agent in addition to i) water and ii) a copolymer as described above, the quenching fluid generally contains from 0.1 to 15 percent, preferably from 1 to 10 percent, more preferably from 4 to 6 percent of such an additional quenching agent, based on the total weight of water, copolymer and additional quenching agent.

40 For quenching a metallic article, it is contacted with the quenching fluid of the present invention. Metallic articles which are suitably quenched according to the method of the present invention preferably are steel, mainly alloy steel or steel of a carbon content of more than 3 percent.

The method of the present invention is also useful for quenching copper, aluminum, nickel, titanium, or alloys, preferably combinations of two or more of the following components: aluminum, tin, palladium, molybdenum, vanadium, chromium, carbon, copper, iron, nickel or silicon.

45 Generally the temperature of the metallic article to be quenched is from 30°C to 1500°C, preferably from 80°C to 1400°C, more preferably from 100°C to 1000°C. The initial temperature of the quenching fluid prior to contact with the metallic article to be quenched preferably is from 10°C to 95°C, more preferably from 20°C to 90°C, most preferably from 30°C to 80°C. In the practice of the quenching process, the metallic article is advantageously agitated in the quenching fluid. Alternatively, the metallic article can be simply dipped into the quenching fluid or can be sprinkled with the quenching fluid.

50 The quenching fluid of the present invention is further illustrated by the following examples which should not be construed to limit the scope of the invention. Unless otherwise mentioned, all parts and percentages are by weight.

55 Examples 1 to 6 and Comparative Examples A to E

The efficiency of the quenching fluid of Examples 1 to 6 and of Comparative Examples A to E is evaluated utilizing a test apparatus commercially available from Drayton Probe Systems Ltd., England, under the trade-

name "Quenchmaster." An Inconel 600 thermal quench probe is utilized in this apparatus. The quench probe is heated to a temperature of 850°C and is then transferred into a preheated sample of the quenching fluid of 2 litre volume. The temperature of the preheated quenching fluid prior to contact with the metallic article to be quenched is listed in Table 1 as bath temperature. The test time period is 60 seconds. The temperature of the quench probe and the time are measured 8 times every second. From the measured data the cooling rate (°C/sec.) vs. temperature is calculated.

In all Examples 1 to 6 a terpolymer of 25 percent acrylonitrile, 25 percent acrylamide and 50 percent acrylic acid is utilized. The terpolymer exhibits a viscosity, as a 16 percent aqueous solution, of about 3000 cps, measured using a Brookfield Viscosimeter, Model LVT, Spindle No. 5 at 20 rpm and 25°C. The terpolymer is mixed with water at various amounts. The blend of water and terpolymer is heated to 40°C or 70°C respectively prior to contact with the metallic article to be quenched.

In comparative Examples A and B a sodium salt of polyacrylic acid having a weight average molecular weight of about 10,000 is utilized. In comparative Examples C and D a sodium salt of polyacrylic acid having a weight average molecular weight of about 20,000 is utilized. In comparative Example E the cooling characteristics of a reference quench oil are measured. The reference quench oil is an undiluted paraffinic mineral oil, free of additives, conforming to the following specification as published by Drayton Probe Systems Ltd.: Kinematic viscosity at 40°C: 19 to 23 cSt; Kinematic viscosity index: 95 to 105; density at 15°C: 0.855 to 0.870 Kg/l and flash point 190 to 210°C.

The percentage of the polymers, based on the total weight of polymer and water, the initial temperature of the polymer/water mixture and the observed cooling parameters, such as the maximum cooling rate, for Examples 1 to 6 and Comparative Examples A to E are listed in Table 1.

Table 1

Example	Concentration ¹⁾ %	Bath Temp. °C	Max. Cooling Rate °C/Sec.	Temp. at Max. Cooling Rate °C	Cooling Rate at 300 °C	Time from Immersion to X °C (sec.)			Fig.
						600 °C	400 °C	200 °C	
1	16	40	11.0	819	-- 2)	27	-- 4)	-- 4)	1
2	16	70	11.0	825	-- 2)	27	-- 4)	-- 4)	2
3	8	40	13.3	818	5.5	21	44	-- 4)	3
4	8	70	13.1	816	-- 2)	22	47	-- 4)	4
5	4	40	16.0	807	8.2	19	38	-- 4)	5
6	4	70	17.9	355	5.3	20	43	-- 4)	6
Comp. Ex.									
A	10	40	41.1	270	36.8	14	21	28	7
B	10	70	44.0	284	42.7	17	35	42	8
C	5	40	47.6	641	15.0	9	16	26	--
D	5	70	39.5	231	18.0	17	33	42	--
E	100 ³⁾	40	47.5	516	6.3	13	21	54	9

1) Percentage of polymer, based on total weight of polymer and water

2) Not measured because even lower than in Examples 3, 5 and 6

3) Undiluted Mineral Oil

4) Not measured because longer than 60 seconds

Table 1 illustrates that the quenching fluids according to the present invention have a considerably lower cooling rate than known polyacrylate/water blends according to comparative Examples A to D and than mineral oil according to comparative Example E. Furthermore, Table 1 illustrates that altering the bath temperature of the quenching fluid of the present invention (see Examples 12, 3-4 and 5-6) has a less significant influence on the maximum cooling rate than altering the bath temperature of the polyacrylate/water blends (see Comparative Examples A and B and C and D). Accordingly, the cooling rates can be better controlled when using a terpolymer/water blend according to the present invention than when using a polyacrylate/water blend according to the state of the art.

In Figure 1 to 9 the curves of the cooling efficiency of the quenching fluids of Examples 1 to 6 and of Comparative Examples A, B and E are illustrated. In all figures curve A indicates the temperature vs. time (in seconds) and curve B indicates the temperature vs. cooling rate ($^{\circ}\text{C}/\text{sec}$).

The comparisons between Figure 1 and Figure 2, between Figure 3 and Figure 4 and between Figure 5 and Figure 6 respectively illustrate that the cooling rates are not substantially influenced by the variation of the temperature of the copolymer/water blend prior to contact with the metallic article to be quenched. This fact allows a good control of the cooling process when utilizing a quenching fluid of the present invention.

The comparison between Figure 7 and 8 (Comparative Examples A and B) illustrates that the cooling rates are substantially influenced by the variation of the temperature of the polyacrylate/water blend prior to contact with the metallic article to be quenched. A large scattering is observed when comparing Figure 7 (40°C bath temperature) and Figure 8 (70°C bath temperature). Similar curves with a large scattering are also observed for the cooling processes according to Comparative Examples C and D.

Examples 7 to 9

The efficiency of the quenching fluid of Examples 7 to 9 is evaluated in the same manner as in Examples 1 to 6. The same terpolymer as in Examples 1 to 6 is utilized. By the addition of the additives set forth below to water and to the terpolymer of acrylonitrile/acrylamide/acrylic acid, the maximum cooling rate of the quenching fluid can be increased. A wide range of cooling rates can be provided by this method. The quenching fluid of the present invention can be adopted to the requirements of the various metallic articles. Accordingly, a very versatile quenching fluid is provided by the present invention.

In Example 7, 2 parts of the terpolymer, 3 parts of sodium hydroxide and 95 parts of water are utilized.

In Example 8, 1 part of the terpolymer, 94 parts of water and 5 parts of a polyether polyol are utilized. The polyether polyol is a reaction product of sorbitol and propylene oxide in a molar ratio of 1:9. In the closed-bottle biodegradability test according to OECD-NR 301-D, 40 percent of the polyether polyol is degraded in 28 days.

In Example 9, 1 part of the terpolymer, 5 parts of the same polyether polyol as in Example 8, 3 parts of sodium hydroxide and 91 parts of water are utilized.

The cooling characteristics of the quenching fluid of Examples 7 to 9 are listed in Table 2. The bath temperature is 40°C in all examples.

Table 2

Example	Max. Cooling Rate $^{\circ}\text{C}/\text{Sec}$.	Temp. at Max. Cooling Rate $^{\circ}\text{C}$	Cooling Rate at 300°C	Time from Immersion to X $^{\circ}\text{C}$ (sec.)		
				600 $^{\circ}\text{C}$	400 $^{\circ}\text{C}$	200 $^{\circ}\text{C}$
7	62.0	521	15.1	15	19	35
8	64.4	316	63.4	17	29	33
9	101.0	419	85.3	14	16	19

In spite of a fast cooling rate at high temperatures, the cooling rate at 300°C is low in Example 7 which is very advantageous.

It can be seen from the foregoing that, at least in its preferred embodiments, the invention is capable of providing a new water-based quenching fluid which has a lower cooling rate than known water-based quenching fluids, and in particular a new quenching fluid which has a maximum cooling rate or a cooling rate at 300°C

respectively, which is not substantially higher than the maximum cooling rate or the cooling rate at 300°C respectively of mineral oil and which, if desired, can be compounded in such a manner that it has about the same or even a lower maximum cooling rate or a cooling rate at 300°C respectively than mineral oil.

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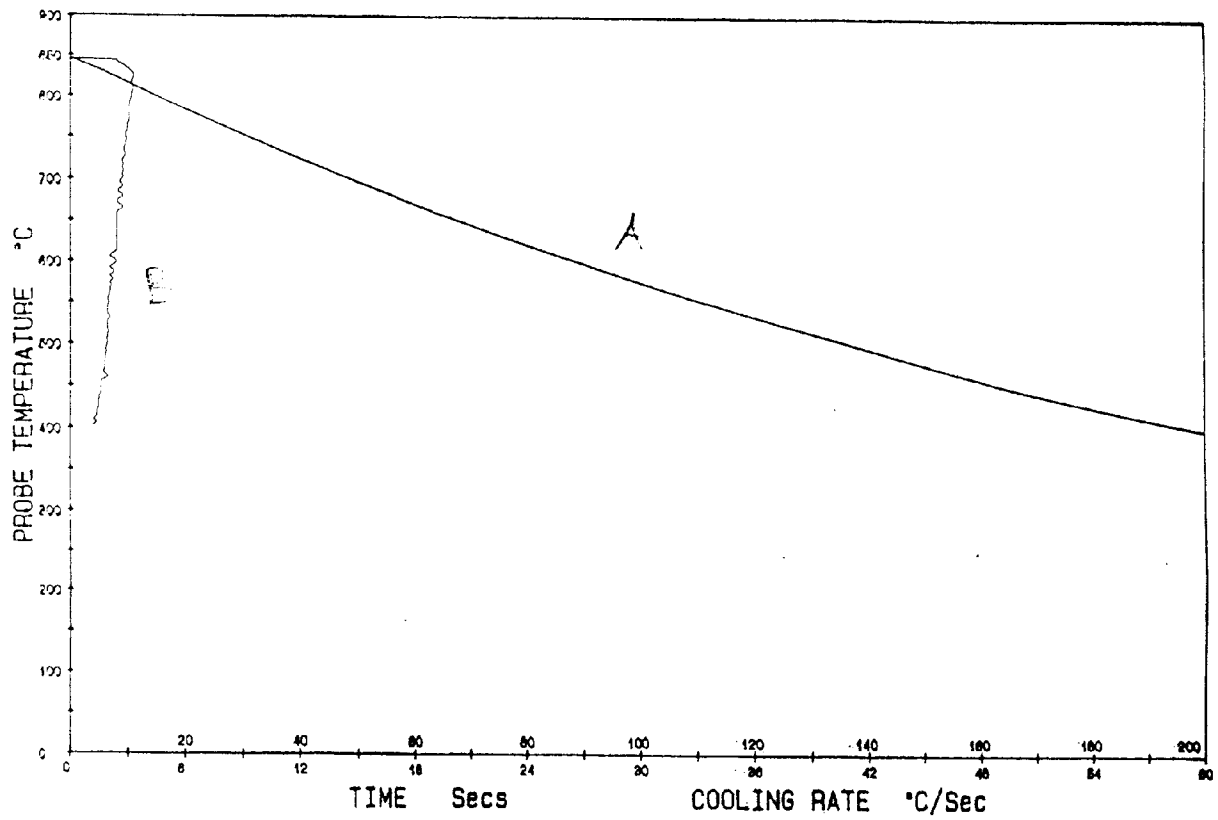
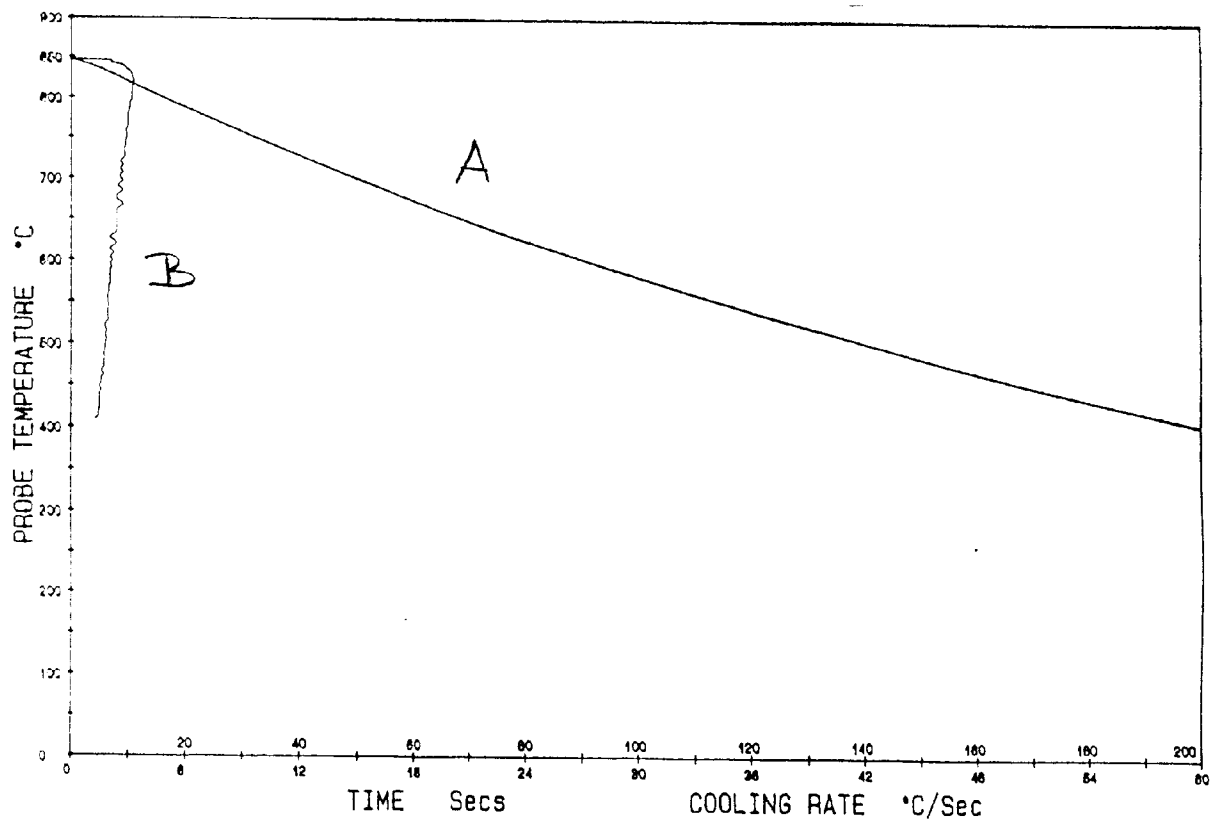
Claims

1. A quenching or cooling fluid comprising
 - i) water and
 - ii) a copolymer containing, in polymerized form, from 30 to 97 percent of an α,β -ethylenically unsaturated carboxylic acid, from 1 to 50 percent of an ethylenically unsaturated amide and from 2 to 69 percent of a hydrophobic monomer, by the total weight of the carboxylic acid, the amide and the hydrophobic monomer.
2. The quenching fluid of Claim 1 wherein the hydrophobic monomer is acrylonitrile, methyl acrylate, methyl methacrylate or vinyl acetate.
3. The quenching fluid of Claim 2 wherein the hydrophobic monomer is acrylonitrile.
4. The quenching fluid of any one of Claims 1 to 3 wherein the ethylenically unsaturated amide is acrylamide.
5. The quenching fluid of any one of Claims 1 to 4 wherein the ethylenically unsaturated carboxylic acid is acrylic acid.
6. The quenching fluid of any one of Claims 1 to 5 wherein the copolymer contains, in copolymerized form, from 35 to 85 percent of the α,β -ethylenically unsaturated carboxylic acid, from 5 to 40 percent of the ethylenically unsaturated amide and from 10 to 50 percent of the hydrophobic monomer, by the total weight of the carboxylic acid, the amide and the hydrophobic monomer.
7. The quenching fluid of any one of Claims 1 to 6 comprising from 0.1 to 40 percent of the copolymer and from 60 to 99.9 percent water, based on the total weight of the copolymer and water.
8. The quenching fluid of Claim 7 comprising from 2 to 20 percent of the copolymer and from 80 to 98 percent water, based on the total weight of the copolymer and water.
9. The quenching fluid of any one of Claims 1 to 8 comprising additionally a polyether polyol being the reaction product of one or more C_{2-4} -alkylene oxides and a polyhydroxy compound containing at least 4 hydroxy groups and at least 5 carbon atoms.
10. A method of quenching or cooling a metallic article by contacting the article with the quenching fluid of any one of Claims 1 to 9.

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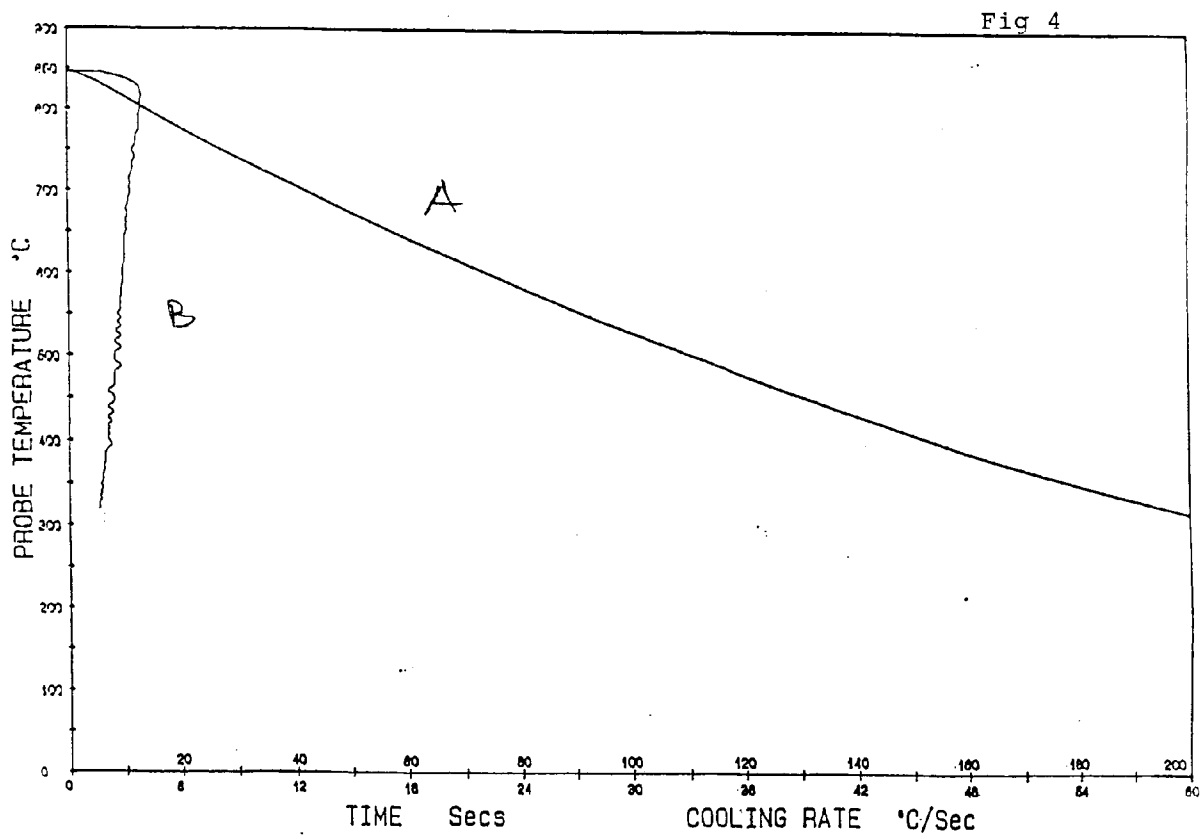
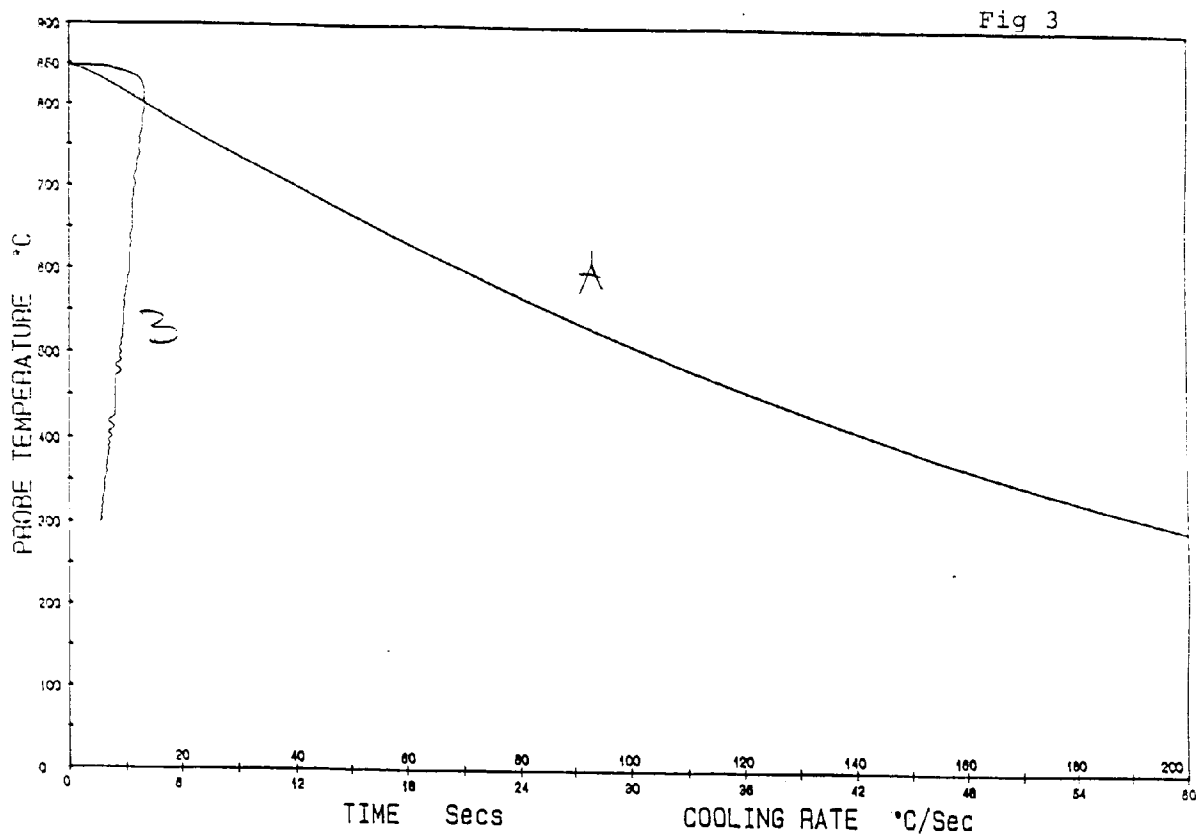


Fig 5

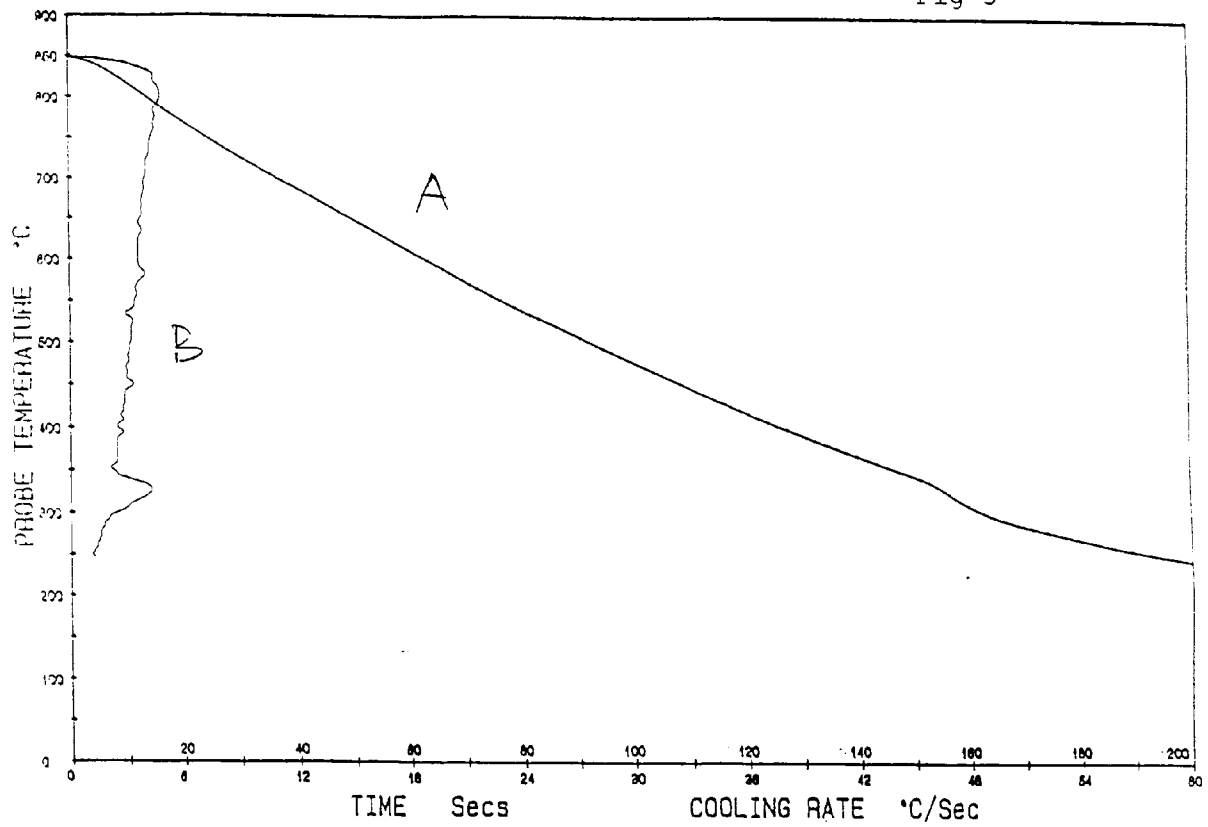


Fig 6

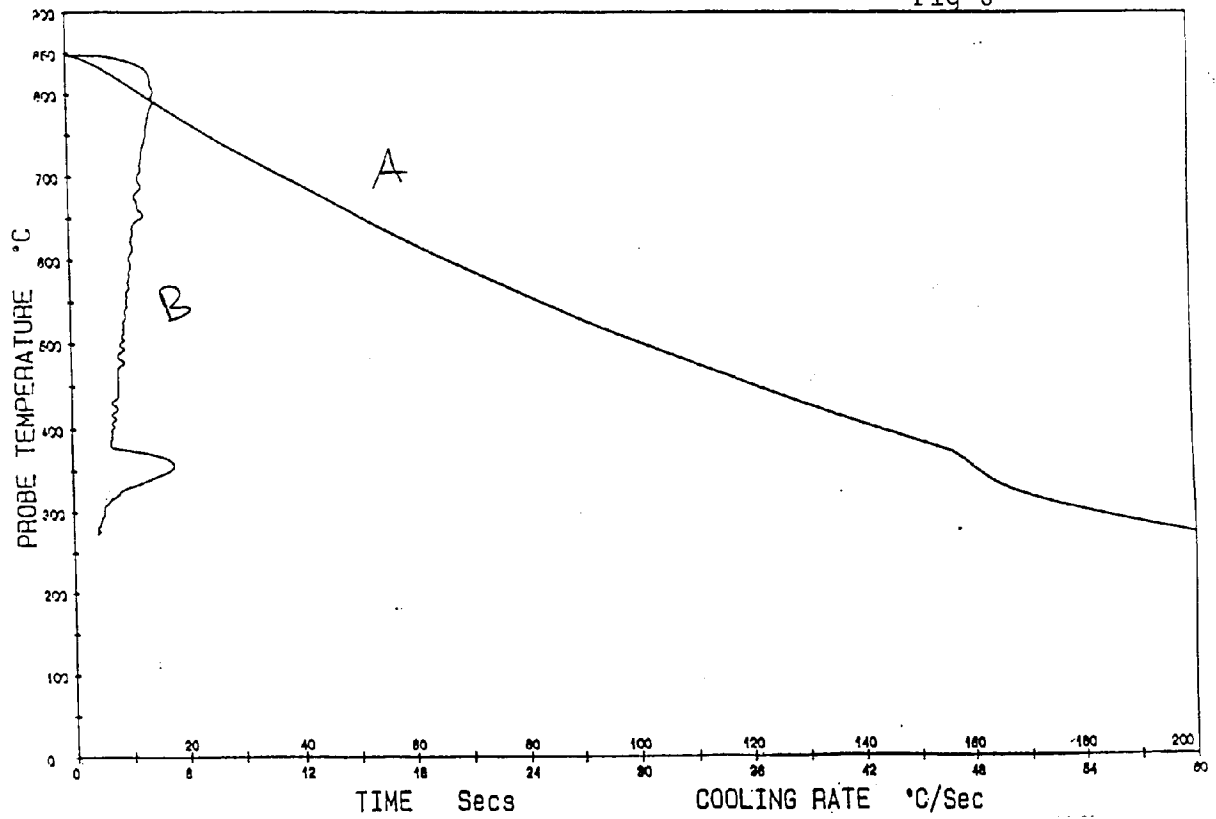


Fig 7

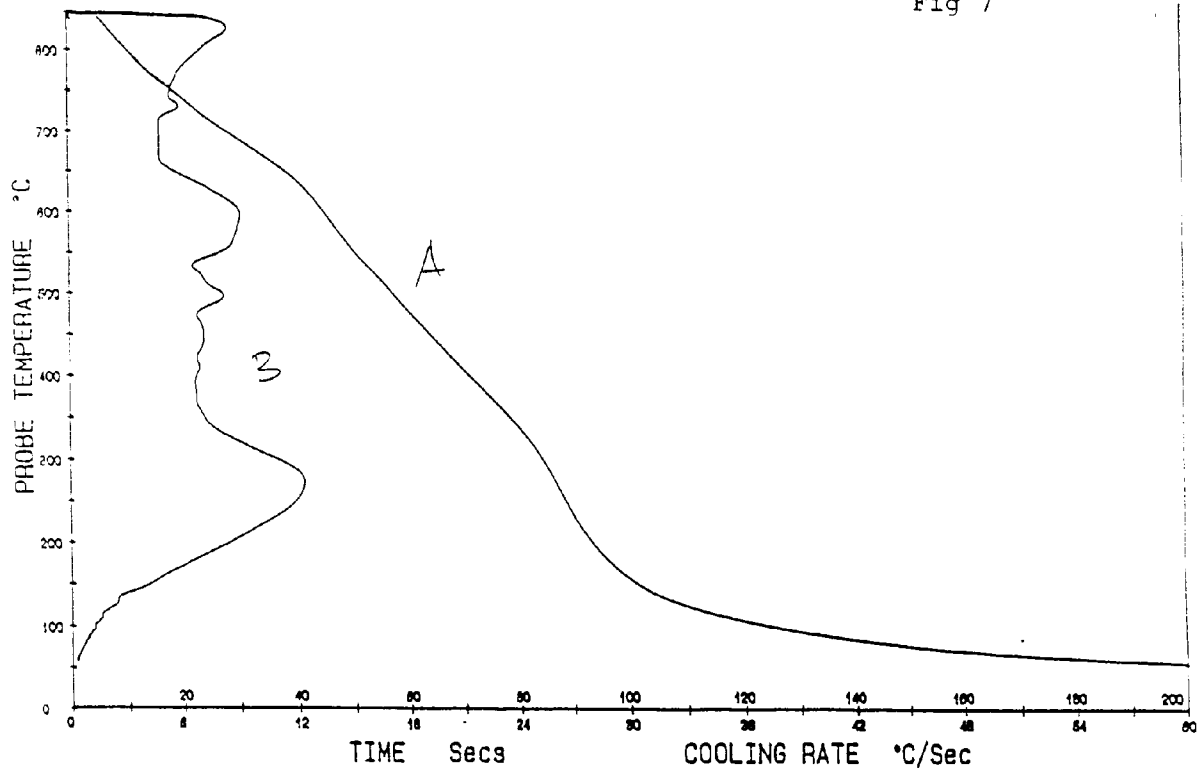


Fig 8

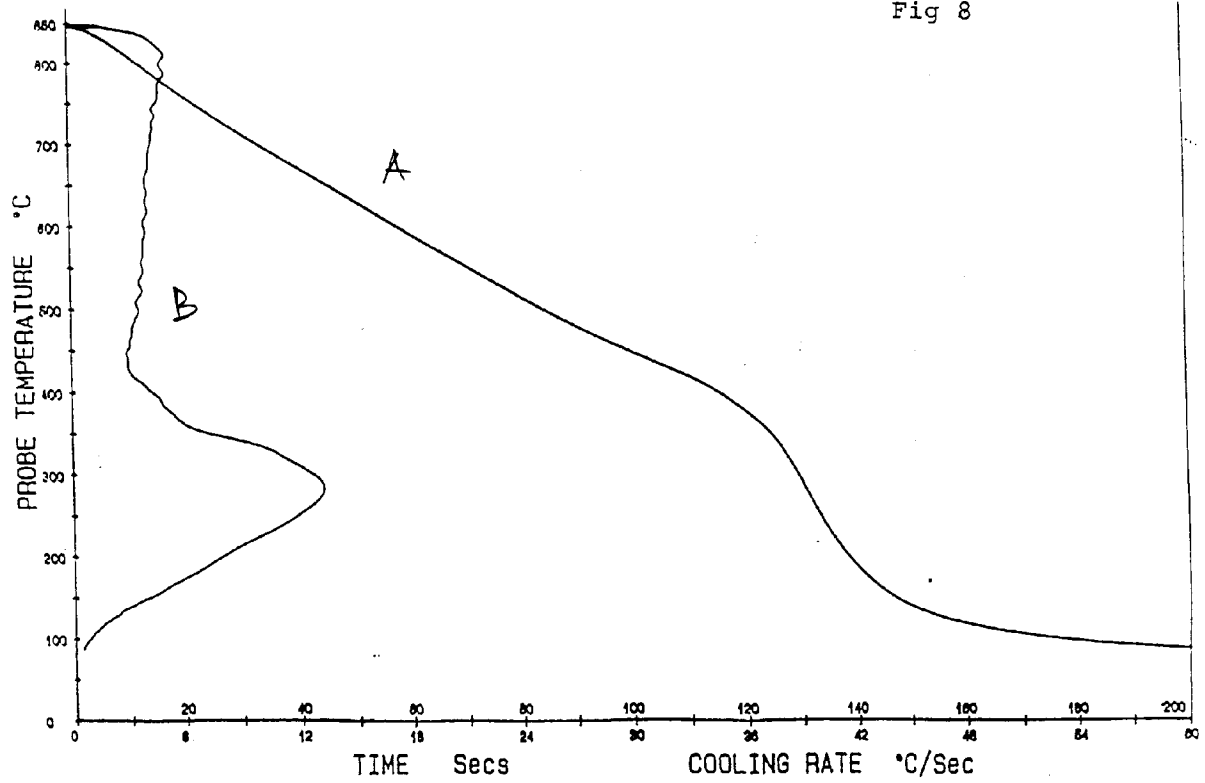
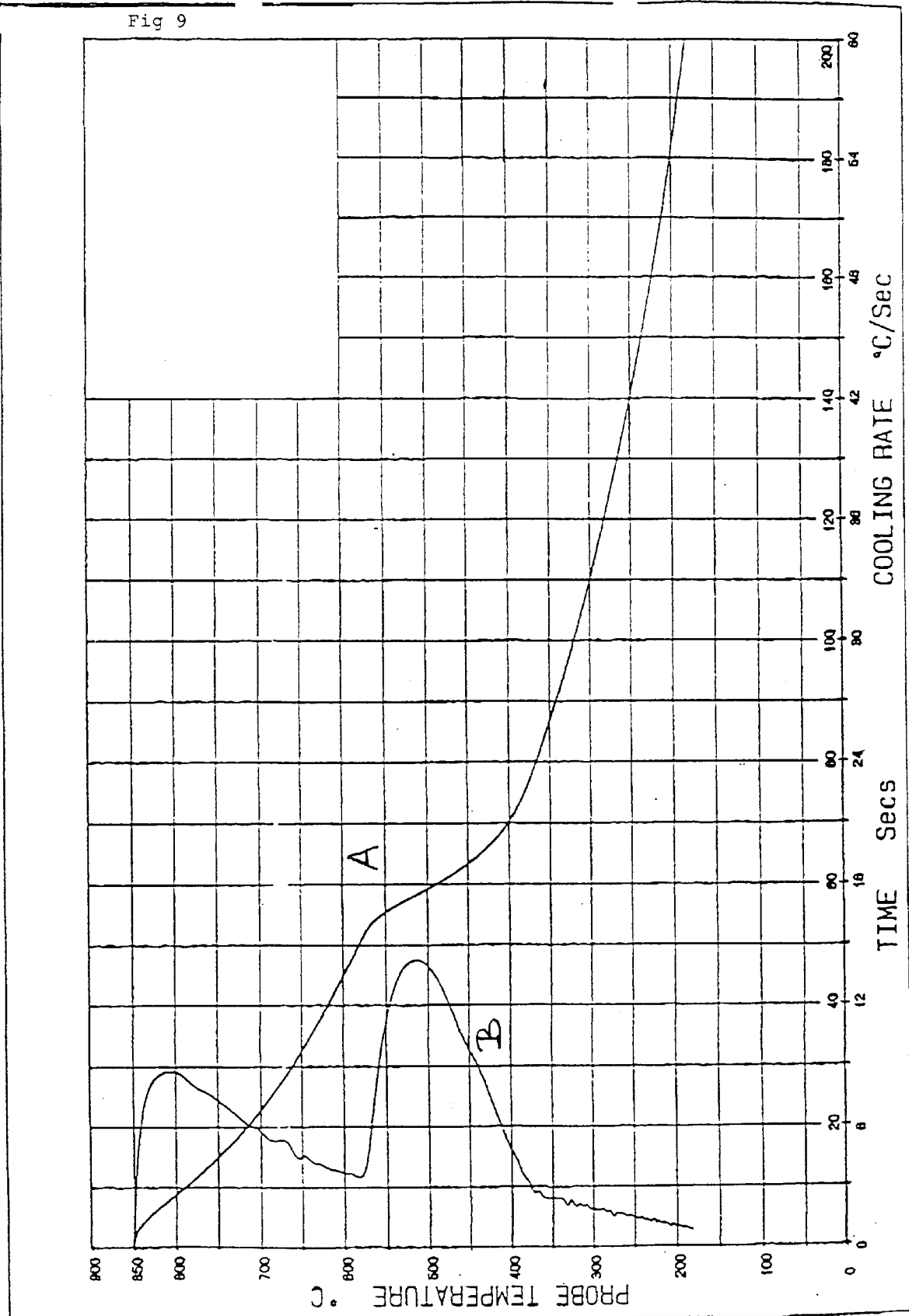


Fig 9





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 93 31 0314

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.5)
A	GB-A-1 163 345 (B.A.S.F.) * the whole document * ----	1,2,5-7, 10	C21D1/60
A	US-A-3 996 076 (T. TOKUUE ET AL.) * column 1, line 46 - column 2, line 57; claim 1; example 5 * ----	1,7,8,10	
A	US-A-5 141 662 (E.M. DEXHEIMER ET AL.) * column 3, line 20 - column 5, line 14; claims 1-4 * -----	9	
The present search report has been drawn up for all claims			TECHNICAL FIELDS SEARCHED (Int.Cl.5) C21D
Place of search THE HAGUE		Date of completion of the search 22 February 1994	Examiner Blasband, I
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			

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