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(54) QUENCHING COOLANT

(57) The subject of the invention is a quenching coolant used in the processes of heat treatment of steel, in particular in the processes of quenching of steel with low hardening capacity, as well as for hyperquenching of other metals and their alloys.

Quenching coolant according to the invention, characterized in it containing from 0.001 to 2.0% by weight of carboxymethylcellulose NaCMC (sodium salt of cellulose glycolic acid), advantageously 0.5% by weight, and contains water in an amount making up to 100% by weight.

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Description

[0001] The subject of the invention is a quenching coolant used in the processes of heat treatment of steel, in particular in the processes of quenching of steel with low hardening capacity, as well as for hyperquenching of other metals and their alloys. State of the art consists of quenching coolants and quenching methods.

[0002] Quenching coolants are used in the processes of heat treatment of metals and metal alloys. These processes frequently require high-speed cooling, not always over the entire temperature range. This applies in particular to such treatments as e..g. quenching of steel. The ranges of temperatures with required high cooling rate depend on the treated metal, its mass and shape.

[0003] The state of the art knows all quenching coolants, including quenching oils, and water-based coolants containing various organic and inorganic compounds which change the cooling capacity of water during the quenching process.

[0004] The patent description with the patent number 159862 presents quenching coolant for steels treated in an endothermal atmosphere, intended for quenching baths, aggregated with a thermal treatment furnace. This coolant is intended for the quenching of steel which were previously carburized, cyanided or austenitized in a protective atmosphere of a furnace with a built in quenching bath. Quenching coolant according to the invention, forming a water solution of glycols and other organic and inorganic compounds, characterized in that it contains silicone oil, advantageously with cross-linked short-chains, in an amount of 5 to 25% by weight, dipropylene glycol in an amount of 20 to 50% by weight, sodium salt of polyacrylic acid with a molecular weight of 10000 - 100000 in an amount of 2 to 5% by weight, sodium salt of acrylic acid copolymer with a molecular weight 300000 - 1000000 in an amount of 0.1 to 2% by weight, polyoxyethylene stearate 1,4-sorbitol in an amount of 0.1 to 2% by weight, sodium salt of ortho-phenylphenol in an amount of 0.05 to 0.2% by weight, ε-caprolactam poly(ethylene oxide) in an amount of 0.05 to 0.3% by weight and water in an amount making up to 100% by weight.

[0005] An agent for the preparation of water-based quenching baths is also known, shown in the patent description 117439. This agent is characterized in that it contains from 30 to 80% by weight, advantageously from 45 to 55% by weight of cationic surfactant or a mixture of such surfactants, advantageously alcoxymethyl pyridinium halogens or quaternary ammonium or pyridinium compounds.

[0006] In the patent description 92610 a quenching bath concentrate was presented, containing 5-50% by weight of polyethylene glycols, 0.05%-0.2% of sodium triphosphate, 0.1-3.0% of sulfonates and water making up to 100%. Quenching bath based on this concentrate provides much better cooling in the upper range of temperatures than known non-oil-based quenching coolants and does not result in "soft stains" on the quenched surfaces.

[0007] The patent description 107518 presents an agent for quenching baths containing 40-80% of ethylene glycol or polyglycol ethers, 0.1-5% of sulfonates, 0.05%-4% of sodium triphosphate, 0.05-4% of colloidal silica as anti-foaming agent and 0.05-4% of poly(vinyl alcohol) in a water solution. The agent's composition is specified by weight. This known agent enables volume quenching and surface induction quenching of low- and medium-alloy carbon steels and retains the ability to adjust cooling rate within a wide range.

[0008] An agent for the preparation of quenching baths is also known shown in the patent description 120857. This agent - intended mainly for high-alloy steels - is fundamentally a mixture of 20-70% by weight of polysaccharides, advantageously starch or its derivatives, and 80-30% by weight of water, and moreover may contain 0.05-5% of acridine compounds, 0.01-8% by weight of sodium hydroxide or tetraborate and 0.01-2% by weight of methyl phenyl silicone oil as anti-foaming agent. Approximately 15% water solution of this known agent is characterized by a much more advantageous cooling curve for high-alloy steels than the cooling curve of OH-70 oil.

[0009] The patent description 151712 presents an agent for the preparation of quenching baths used in particular for high-grade tool steels. The agent contains 10-80 parts by weight of polyacrylamide with high degree of polymerization, 0.05-10.5 parts by weight of triethanolamine, up to 5 parts by weight of formaldehyde and 20-90 parts by weight of water.

[0010] A quenching agent is also know, presented in the patent description 152073 - it forms a water solution from 2 to 10% of anionic polyacrylamide with high degree of polymerization, from 0.2 to 2.5% formaldehyde, from 0.5 to 5% of alcali metals polyphosphates or phosphates or phosphoric acid and from 0.5 to 7% of triethanolamine.

[0011] Moreover an agent is known for preparing of quenching baths for surface quenching of steel. The agent is a water solution containing 20-40 parts by weight of triethanolamine, 10-45 parts by weight of ethylene glycol, 5-20 parts by weight of boric acid, 5-20 parts by weight of sodium tetraborate, 0.5-1 part by weight sodium tripolyphosphate and 0.05-1 part by weight of formaldehyde.

[0012] In the patent description 145784 a quenching coolant was presented containing 10-50% by weight of non-ionic polyacrylamide with high degree of polymerization, 50-90% by weight of water, 0.1-1.5% by weight of sodium* hydroxide and as anti-corrosion additive 1-5% by weight of sodium hexametaphosphate.

[0013] An agent for the preparation of water-based quenching coolant was also demonstrated, described in the patent description 136702. This invention is characterized by consisting of glycerine in an amount of 61-80% by weight, ethylene glycol in an amount of 1-20% by weight, polymerized sulphate free water solution of 6-8% polyacrylamide in an amount of 2-25% by weight and anhydrous sodium carbonate in an amount of 0-6% by weight in the solution of the agent.

[0014] The patent description 86772 presents a method for preparing a quenching bath concentrate, characterized in that 1 to 17% by weight of polyvinyl alcohol, 0.5 to 60% of glycerine and 30 to 95% by weight of water are stirred in a stirrer of any type or using ultrasound, until a uniform consistency of the concentrate is obtained over its entire volume, and then is heated to a temperature of 40 to 100 °C.

[0015] Various types of coolants are also know, which are polymer solutions, the attractiveness of which results from their intermediate cooling rate compared to oil and water, and an important advantage of water polymer solutions is their non-inflammability, which significantly improves operational safety in the quenching shop.

[0016] Cooling of steel in a liquid from austenitization temperature to the environment temperature is performed with a varying cooling rate. In the tested coolants (water, oils, polymer solutions) usually three main ranges of cooling rate changes are observed for a probe heated to 850 °C:

- evaporation phase
- bath boiling stage and
- convection heat exchange phase.

[0017] During the evaporation phase, which occurs right after immersion in a quenching bath, around the quenched item a near-surface steam layer is created, which forms i an insulation layer for the heat exchange process, and in this period the rate of heat transfer is very low. The period of evaporation ends at Leidenfrost temperature, below which cooling is accompanied by the boiling of coolant. With the lowering of the item's temperature the coolant liquid starts to contact the probe surface, and bubbles of boiling liquid start to appear, breaking away from the surface. Boiling decreases, and finally disappears, and then the quenching coolant liquid contacts the entire product without bubbles caused by boiling - this is the period of convection heat exchange (without boiling) when the heated layers of the surface liquid raise upwards in the bath. The diagram of temperature changes for individual periods was presented on **fig. 1** and **2.**

[0018] The aforementioned curves may be described using the following basic parameters, that is:

- highest cooling rate - CRmax, °C/s
- temperature at which the highest cooling rate occurs - T(CRmax), °C
- boiling point (Leidenfrost temperature) - Tvp, °C
- convection point - Tcp, °C
- cooling rate at 300 °C - CR300, °C/s
- time for reaching a temperature of 600 °C - Time600, s
- time for reaching a temperature of 400 °C - Time400, s
- time for reaching a temperature of 200 °C - Time200, s

[0019] The description of coolant's ability to collect heat the most popular method defined in the ISO 9950 standard is used [T. Holm, P. Olsson, E. Troell - Steel and its Heat Treatment. A Handbook. Swerea IVF, Sweden, 2012]. The shape and dimensions of the probe used to measure the coolant's heat collection capacity according to the ISO 9950 standard and individual phases of behaviour of typical polymer after a probe is immersed in it was presented on Fig. 3.

[0020] In the case when the coolant is a polymer solution, then the analogous cooling phases described above are supplemented with the deposition of polymer film near the surface of the cooled metal. The deposition of the polymer film is related to the inversion of the polymer solution's concentration. This may be described in the most simple manner that with the increase of the solution temperature after passing through a specific maximum solubility temperature, the water solubility of polymer starts to decrease and it precipitates out of the solution. Many publications describe this phenomenon in polymer solutions [L. Mandelkern - Crystallization od Polymers. Second Edition, Cambridge University press, 2002].

[0021] Transition from the evaporation phase to boiling phase is frequently accompanied by a significant sound effect, which results from the accumulating steam bubbles violently breaking the polymer film surrounding the metal. The polymer film is a bad heat conductor, thus it reduces the speed of heat energy transfer into the coolant. The thicker the film (which occurs at higher polymer concentrations), the slower heat transfer is. This demonstrates that it is possible to adjust the characteristics of the coolant by adjusting the solution's concentration, which is used in practice.

[0022] Inhibition of heat transfer through the polymer film in the initial cooling period (during the evaporation phase) has a negative impact and is usually undesirable, since it is advantageous to lower the temperature as fast as possible in the range of 850 to 450 °C, to bypass the "nose" of the initial change on the CTPc diagram. One of the solutions used to eliminate this negative factor is intense stirring of the polymer bath. The flow of liquid rips away the polymer and steam layer, which increases the cooling speed.

[0023] Below the temperature of approx. 450 °C it is advisable to reduce the heat transfer, which enables the minimisation of quenching deformations and the risk of quench cracking is decreased. That is why the polymer film plays a very important role during the convection phase and its formation in this cooling period is highly desirable.

[0024] Based on the conducted analysis it was established that a universal quenching coolant suitable for all currently known uses does not exist, which results from the fact that each material has other characteristics, requiring different cooling rates and other temperature ranges for intense cooling.

[0025] Since heat treated metals and alloys differ significantly from each other, an appropriate coolant is selected to each product. There is no quenching coolant which is suitable for all metals or their alloys. Therefore in practice the coolants are matched to a specific heat treated material, therefore a wide range of coolants is used, such as: salt and alkaline water solutions, water, quenching oils (usually synthetic), polymer solutions, gasses, molten salts and molten metals. These coolants may be used with various cooling methods, e.g. by immersion in coolant baths, by liquid spraying, by gas blowing, in presses, in fluidised beds etc.

[0026] The fastest known immersion coolants are salt and alkaline water solutions. The coolant characteristics of a 10% NaCl salt water solution are presented on Fig. 4. In this case the maximum cooling speed of 260 °C/s was obtained at the temperature of 720 °C already. The lack of evaporation period in the initial quenching period, right after the immersion of the probe in the quenching bath should also be noted.

[0027] When analysing the obtained results, the lack of difference in the curves for a stirred solution - red line, and a stationary solution - blue line should also be noted (own research).

[0028] The method of cooling and the coolant are selected not only for economic reasons, but also in order to minimise deformations after heat treatment. Therefore for non-alloy steels undergoing quenching, a rapid course of quenching from austenization point to the martensitic transformation point would be desirable, and further course of cooling should be performed at a lower rate, reducing the post-quenching stresses and deformations.

[0029] Cooling in a salt solution or in pure water is frequently not a good solution and leads to the occurrence of quenching cracks, whereas the use of one of the available quenching oils lead to an insufficient cooling rate. The polymer solutions turned out to be an intermediate medium between water and oils, since they have varying cooling characteristics. They do not have the main disadvantage of oils, that is, the inclination to ignition and smoking. The polymer solutions are therefore safer to use and allow the adjustment of the heat collection ability by changing the solution's concentration.

[0030] In case of the use of quenching coolants known from the state of the art the fact that during the evaporation phase, that is, right after the immersion of the quenched element in the quenching bath a steam layer forms around it, insulating against heat transfer, and causing a very low heat transfer rate is a significant problem.

[0031] The solution according to the invention eliminates the drawbacks and disadvantages known from the state of the art.

[0032] The essence of the invention, which is a quenching coolant made as a water solution, consists of it containing from 0.001 to 2.0% by weight of carboxymethylcellulose NaCMC (sodium salt of cellulose glycolic acid), advantageously 0.5% by weight, and contains water in an amount making up to 100% by weight.

[0033] It is advantageous when the solution contains distilled water, whereas it is particularly advantageous when the quenching coolant contains germicidal and fungicidal agents, most advantageously in the form of oxazolidine - MBO, in an amount of 0.05 to 0.15% by weight, most advantageously 0.1% by weight.

[0034] The use of the solution presented in the invention enables the following technical and utility effects:

- stabilization of process parameters,
- improvement of heat collection parameters,
- increase of the cooling rate within the temperature range of 850°C to 300°C,
- optimisation of process costs with simultaneous improvement of the quenching process effectiveness,
- decreased negative environmental impact.

[0035] According to the invention the main ingredient for the biopolymer polyelectrolyte quenching coolant is the sodium salt of cellulose glycolic acid, that is, carboxymethylcellulose (NaCMC), which is an amorphous substance, easily dissolved in hot and cold water, forming stable solutions - in such an aquaeous solution NaCMC is a polyelectrolyte (a polyacid).

[0036] Carboxymethylcellulose is a semi-synthetic cellulose derivative widely used in the food industry (ingredient with the symbol of E466) as a thickener, emulsifier, dietary fibre, and in pharmaceutical processing used in an amount of 2-6% as a bonding agent for wet pelleting, and in tablets as a disintegrant. Carboxymethylcellulose is environmentally friendly and biodegradable. The substance is not classified as hazardous. It is also used in the manufacturing of ointments and a hydrogel base. Moreover, carboxymethylcellulose has a wide variety of other uses, e.g. in the manufacture of paints (as a thickener) or in oil drilling.

[0037] In order to avoid undesirable growth of bacteria and fungi introduced with the water, it is recommended to use distilled water for the preparation of polymer solutions. Carboxymethylcellulose is relatively resistant to the action of microorganisms, however it may undergo depolimerisation. Carboxymethylcellulose solutions therefore may demonstrate a propensity for the growth of bacteria and fungi, therefore just as for quenching oils and other polymers being sold, it is recommended to use an additive or additives which inhibit the corrosion of quenching baths and microbial growth. One of the solutions is the use of an additive containing oxazolidine - MBO, the addition of which to the solution in an amount of 0.05 to 0.15% by weight should sufficiently protect the bath against the adverse effect of microbial growth.

[0038] Taking the aforementioned into account, the quenching coolant in the example implementation, prepared as a water solution, contains:

- 0.5% by weight of carboxymethylcellulose NaCMC (sodium salt of cellulose glycolic acid)
- 0.1% by weight of oxazolidine - MBO (germicidal and fungicidal agent)
- distilled water making up to 100% by weight

[0039] The tendency towards sedimentation of various polymer solutions means that the polymer bath should be constantly stirred, in order to maintain approximately uniform properties during use. Not stirring the bath will result in a drastic change to the solution's characteristics in the initial range of cooling.

In reference to the solution according to the invention it should be noted that the sodium salt of cellulose glycolic acid (NaCMC) present in powder form is easily soluble in both cold and hot water, whereas in concentrations above 2% kinematic viscosity increases significantly. NaCMC poured into water rapidly swells, whereas in high concentrations the formation of clumps may be observed, which require intensive stirring of the prepared solution in order to be distributed.

[0040] The conducted tests indicate that for a NaCMC concentration in the range of 0.001% to 2% the quenching coolant according to the invention is characterized by a much better stability and rigorous stirring is not a critical condition for maintaining its uniformity. Due to the requirements of the standard and for the purposes of comparison with other studies, during the tests of the quenching coolant according to the invention the stirring of bath was used.

[0041] The tests intended to verify the industrial use of the invention were conducted during the performance of the quenching process for, among others, SB7 spring fasteners used to attach railway rails to sleepers. The ivf SmartQuench instrument was used for the tests, equipped with an additional bath for the stirring of polymer liquids with adjustable speed - according to the ASTM D 6482 standard. The tests were conducted using moving liquid, at a constant stirrer rotational speed of 1000 rpm.

[0042] The example quenching was performed under production conditions on SB7 spring fasteners. These fasteners were manufactured with 51Si7 grade medium-carbon steel, that is, with added silicon. The rods used for manufacturing were 16 mm in diameter.

[0043] They were quenched using traditional technology, in a polymer solution popular on the market, and after quenching were subjected to high tempering over 1 hour. The main requirements for such springs are martensitic structure without proeutectoid ferrite and hardness after heat treatment in the range of 42-46 HRS.

[0044] The quenching was conducted using two versions of the solution, with a NaCMC concentration of respectively 0.3% and 0.5%, which form example implementations.

[0045] In case of quenching in a polymer solution with a concentration of 0.3% after quenching and tempering the following hardness measurement results were obtained: 44, 44 and 45 HRC. The examination of structure using a scanning microscope have demonstrated the presence of martensite tempered without any trace of proeutectoid ferrite, which indicated that desired and correct results were obtained. Characteristics of quenching coolant with a NaCMC concentration at a level of 0.3% was presented on fig. 5.

[0046] The second example implementation is quenching in a polymer solution with a NaCMC concentration of 0.5%. After quenching and tempering the following hardness measurement results were obtained: 46, 46 and 46 HRC. The examination of structure using a scanning microscope have demonstrated the presence of martensite tempered without any trace of proeutectoid ferrite, which also indicated that desired and correct results were obtained.

[0047] The conducted tests demonstrate that a polymer solution in accordance with the invention has a more advantageous characteristic compared to a typical polymer solution. A comparison of selected parameters subjected to analyses is presented in **Table 2.**

Tab. 2.

A list of selected parameters for compared polymer solutions: "typical" and according to the invention.				
Selected parameters	"Typical" solution		Solution according to the invention	
	unstirred	stirred	unstirred	stirred
Leidenfrost temperature, $\mathbf{T_{vp}}$, °C	728	842	843	840
Max. cooling rate $\mathbf{CR_{max}}$, °C/s	72	139	200	199
Maximum cooling rate temperature **T** (CR_{max}), °C	583	713	586	567

(continued)

A list of selected parameters for compared polymer solutions: "typical" and according to the invention.				
Selected parameters	"Typical" solution		Solution according to the invention	
	unstirred	stirred	unstirred	stirred
Cooling time to a temperature of 200 °C, $Time_{200}$, s	13.11	9.48	6.01	6.18

[0048] Based on the conducted tests the lack of stable characteristics in case of a "typical" solution was established. It has acceptable properties only when the solution is being stirred. For a stationary bath the heat collection parameters undergo significant change. In this aspect the solution according to the invention has more stable parameters. Moreover, it has a much higher cooling speed, and what is important, this rapid decrease of temperature begins before reaching the earliest point of phase transitions in steel. This enables obtaining martensitic structures without proeutectoid ferrite educing on the former austenite's grain boundaries. The lack of uniform characteristics of the quenching coolant in a stationary state (unstirred) and in a moving state (during the stirring of bath) may result in non-homogenous properties of the quenched details, if the conditions of fluid flow in the quenching bath will be non-uniform. This case is present most frequently and may be the cause of lowered quality of production.

[0049] The use of quenching coolant according to the invention, in the form of a carboxymethylcellulose based polymer solution with a concentration of 0.3% (quenching performed under production conditions) allowed obtaining better results then the use of solutions known from the state of the art. After quenching and tempering the hardness in the following range was obtained: 44-45 HRC. The examination of structure using a scanning microscope have demonstrated the presence of martensite tempered without any trace of proeutectoid ferrite, which indicated that desired and correct results were obtained after the quenching using a new polymer solution with a concentration of 0.3%.

[0050] As a result of conducted tests no quenching cracks were found on the surface of details subjected to quenching. The example structures were shown on Fig. 6.

[0051] The conducted tests indicate that the use of quenching coolant acc. to the invention allows the effective conducting of heat treatment process for steels with low hardening capacity, since the main advantage of this coolant is the very high cooling speed in the upper quenching range, that is, between 850°C and 300°C.

Claims

1. Quenching coolant made as a water solution, **characterized in** it containing from 0.001 to 2.0% by weight of carboxymethylcellulose NaCMC (sodium salt of cellulose glycolic acid), advantageously 0.5% by weight, and contains water in an amount making up to 100% by weight.

2. Quenching coolant acc. to claim 1 **characterized in that** the solution contains distilled water.

3. Quenching coolant acc. to claim 1 or claim 2, **characterized in that** the solution contains germicidal and fungicidal agents, advantageously in the form of oxazolidine MBO, in an amount of 0.05 to 0.15% by weight, most advantageously 0.1% by weight.

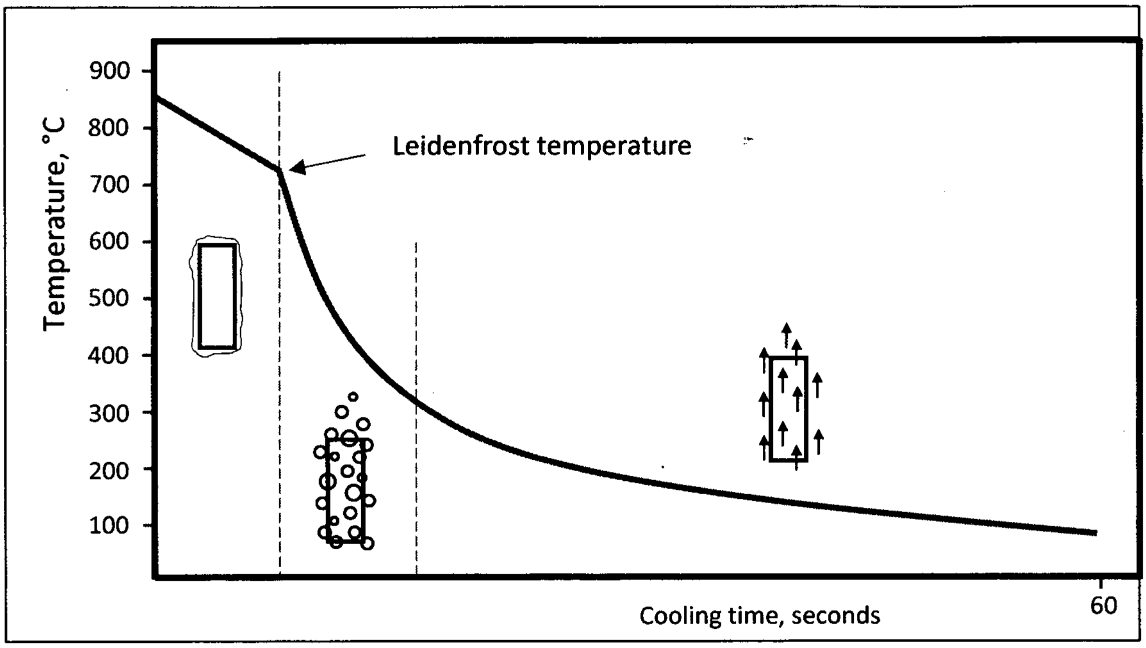


Fig. 1. The diagram presenting typical periods occurring usually after the immersion of the tester in the quenching coolant.

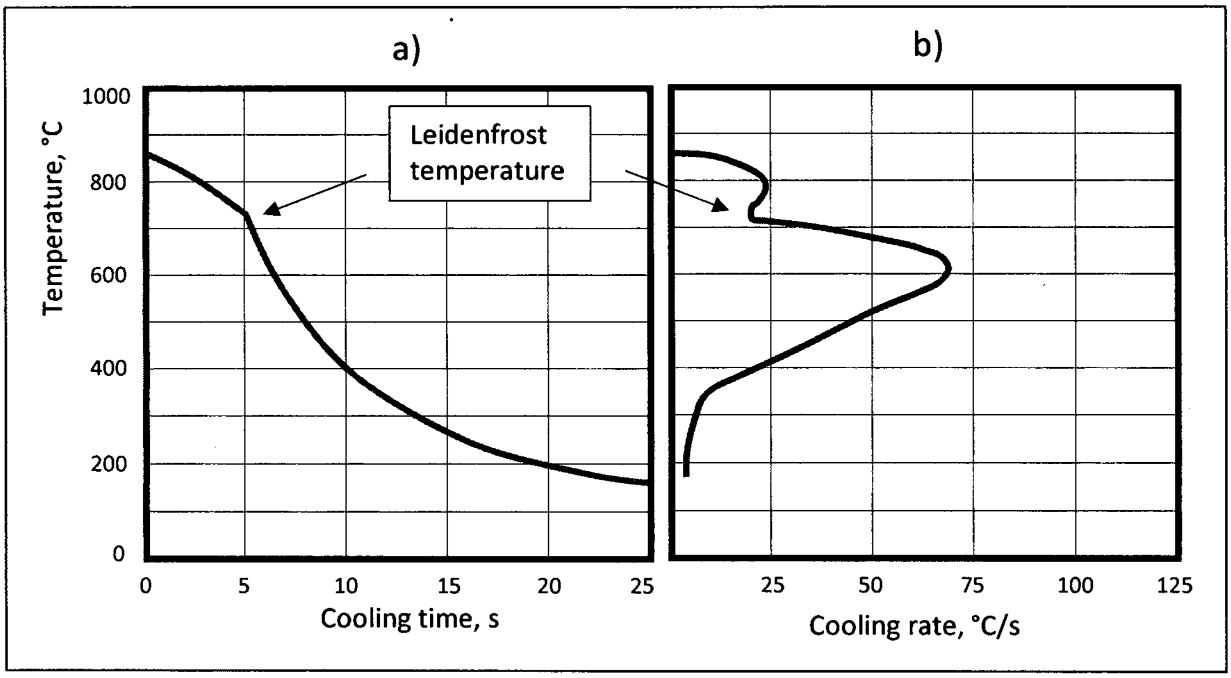


Fig. 2. Schematic presentation of two version of the same cooling process:
a) Curve of probe temperature change over time and
b) after differentiation of the curve from Fig. 2a) the curve of temperature decrease depending on the cooling rate is obtained.

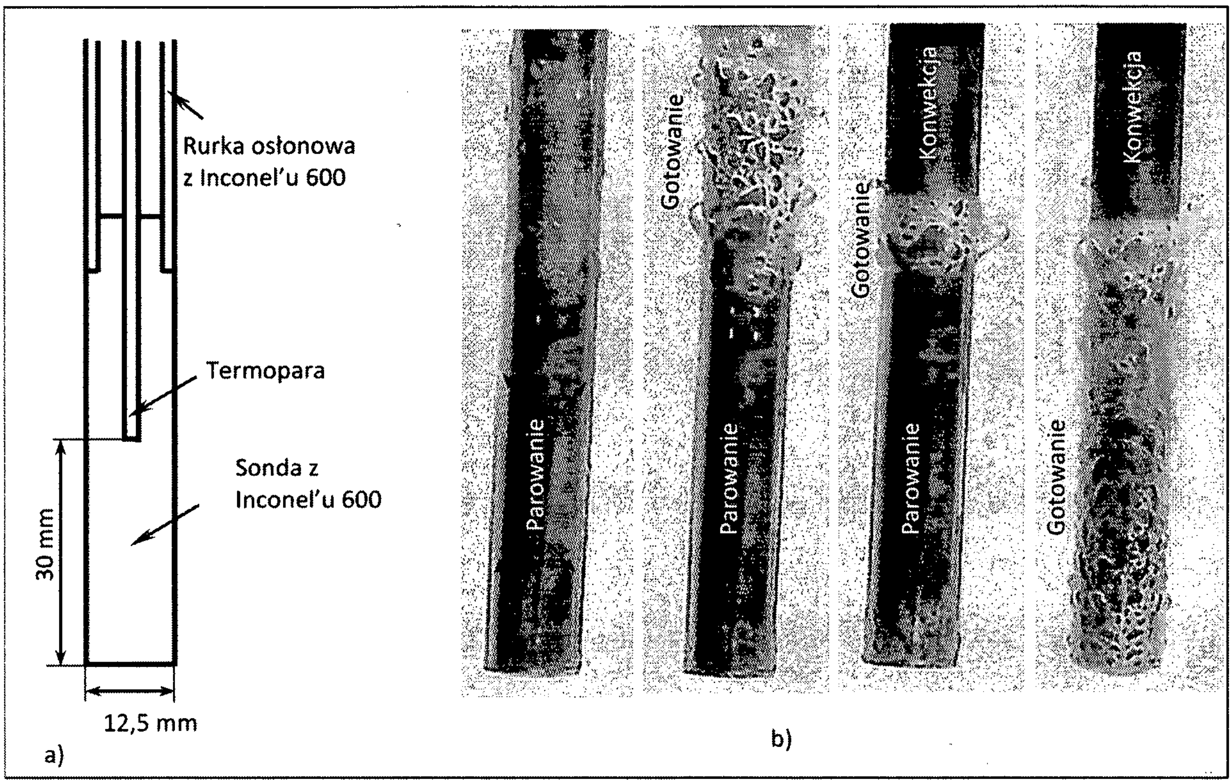
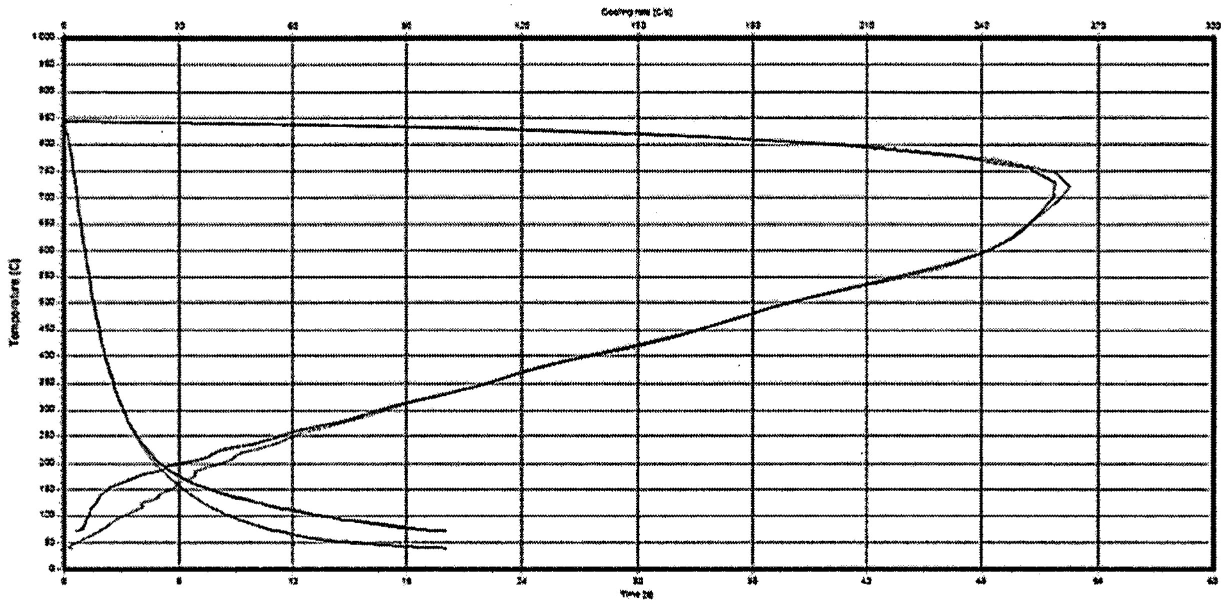


Fig. 3. The probe used to measure the coolant's heat collection capacity according to the ISO 9950 standard

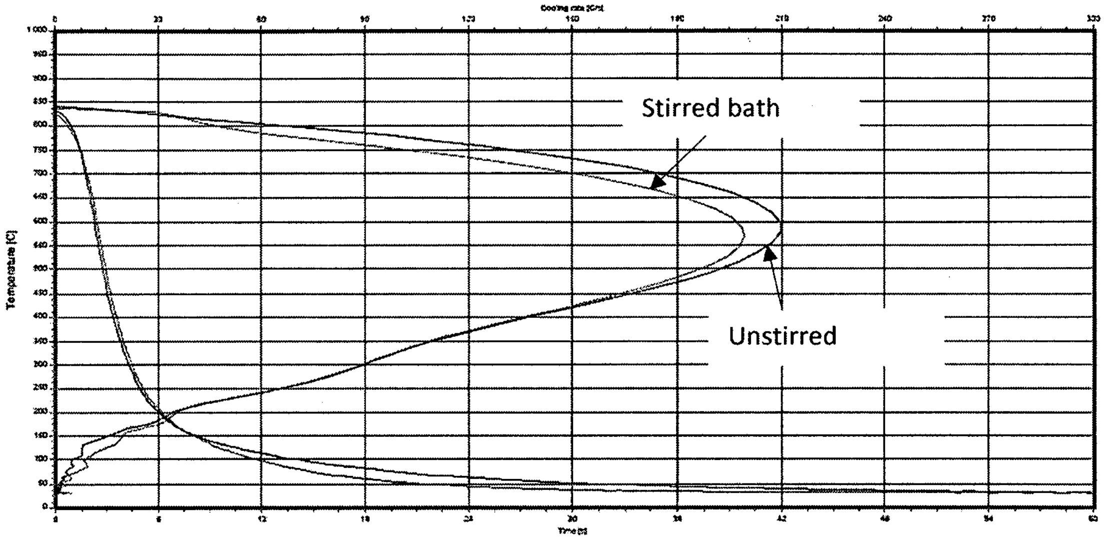
a) shape and dimension of the probe,

b) individual phases of behaviour of typical polymer after the immersion of the ivf SmartQuench probe — in a still bath.



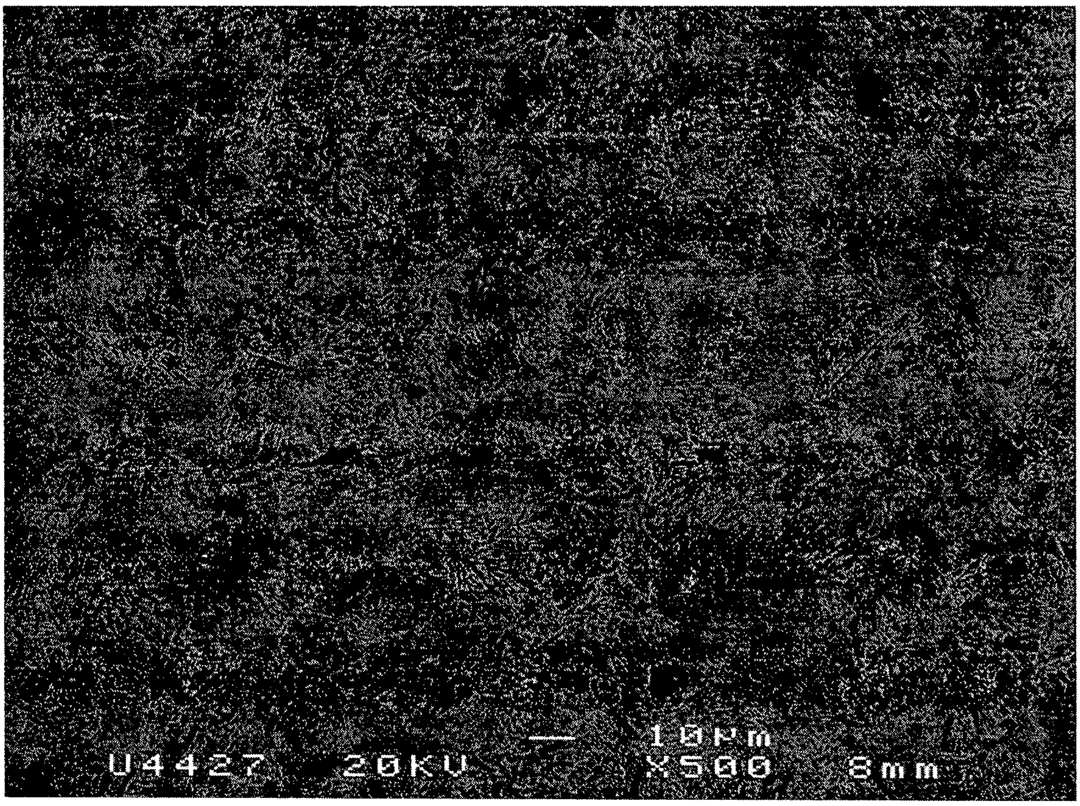
10% NaCl in H_2O	Parameter							
	CR$_{max}$	**T**(CR_{max})	**T**$_{vp}$	**T**$_{cp}$	**CR**$_{300}$	$Time_{600}$	$Time_{400}$	$Time_{200}$
	°C/s	°C	°C	°C	°C/s	s	s	s
Stirred	263	724	842	182	85	1.08	2.15	4.78
Unstirred	259	721	844	164	82	1.11	2.19	5.02

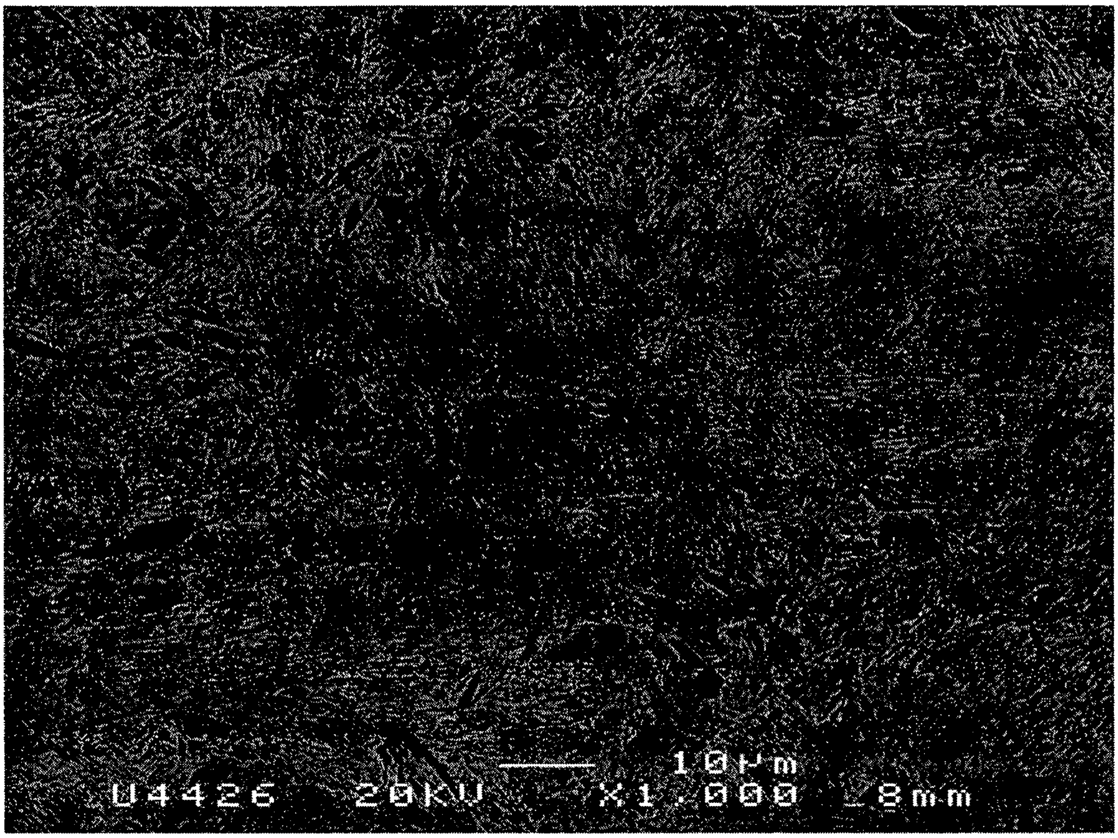
Fig. 4. The changes to heat collection by a 10% NaCl water solution. Measurement performed with the ivf SmartQuench instrument.



New polymer solution 0.3%	Parameter							
	CR_{max}	$T(CR_{max})$	**T_{vp}**	**T_{cp}**	**CR_{300}**	$Time_{600}$	$Time_{400}$	$Time_{200}$
	°C/s	°C	°C	°C	°C/s	s	s	s
Stirred	199	567	840	149	89	2.44	3.57	6.18
Unstirred	210	586	843	152	89	2.29	3.39	6.01

Fig. 5. Characteristics of quenching coolant with a concentration of 0.3%.




10µm
U4426 20KV X1,000 8mm

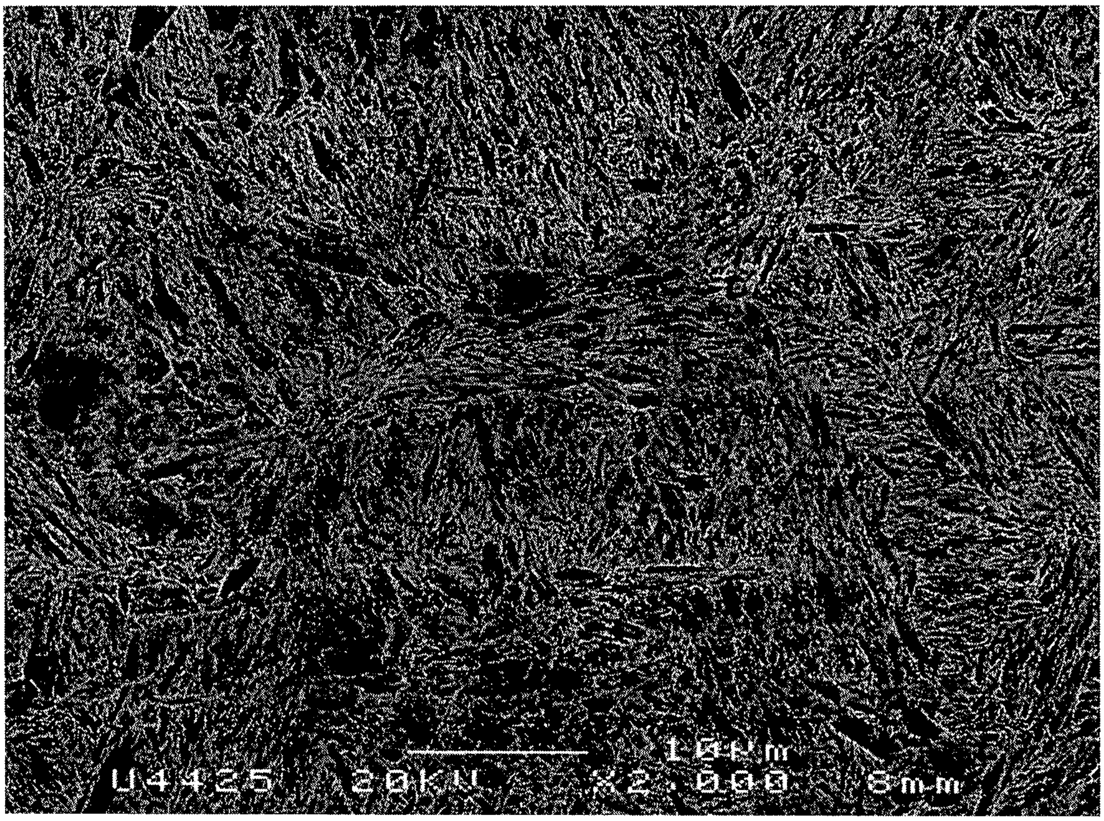

10µm
U4425 20KV X2,000 8mm

Fig. 6. The structure of the SB7 fastener under various magnification, quenched under production conditions in the new polymer solution with a concentration of 0.3%.

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EUROPEAN SEARCH REPORT

Application Number
EP 19 46 0032

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	ZAKHAROV A V ET AL: "STUDY OF THE POSSIBILITIES OF USING POLYMER AGENT NA-CARBOXYMETHYL CELLULOSE FOR QUENCHING RAILS AND RAIL FASTENING COMPONENTS", METAL SCIENCE AND HEAT TREATMENT, SPRINGER, NEW YORK, NY, US, vol. 33, no. 3 / 04, 1 March 1991 (1991-03-01), pages 294-299, XP000272876, ISSN: 0026-0673, DOI: 10.1007/BF00776438	1-3	INV. C21D1/60
Y	* pages 1-3; figure 1; tables 1-3 * -----	3	
Y	CN 104 263 886 A (CHINA PETROLEUM & CHEMICAL) 7 January 2015 (2015-01-07) * claims 1, 5; tables 1,2 * -----	3	
Y	US 2017/247633 A1 (HASEGAWA MAYU [JP] ET AL) 31 August 2017 (2017-08-31) * paragraphs [0035] - [0037] * -----	3	
Y	CN 108 300 924 A (JINJIANG XINCHENG VEHICLE PARTS CO LTD) 20 July 2018 (2018-07-20) * claims 4, 6; examples 1-3 * -----	3	TECHNICAL FIELDS SEARCHED (IPC) C21D

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	16 October 2019	Tsipouridis, P

CATEGORY OF CITED DOCUMENTS

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