

# On Discovered Unusual Effect Taking Place during Quenching in Polymer Solutions

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**Abstract** - In the paper, the unusual effect is considered and explained based on the existing self-regulated thermal process taking place on the insulated metal surface and the thickness of the insulating layer varying during quenching. The discovered effect consists in forming a “shoulder” on the metal surface cooling curve, which in many cases is above the martensite start temperature  $M_s$ . Such effect lasts relatively a long time and slightly varies versus time. The discovered effect can be successfully used for performing an original austempering process via cold liquids, which was for the first time patented in Ukraine. The new technology, when implemented, saves energy, makes the process less costly, and is environmentally green.

## I. INTRODUCTION

A long ago, in 1983, it was discovered by the author of the current paper a “shoulder” formation during quenching probes in cold polymer solutions. At the beginning were the thoughts that something wrong was with the thermocouple instrumentation on the probe surface. After many careful tests and careful thermocouples instrumentation, author came to the conclusion that “shoulder” is true. It was prepared a report on unusual effect which was observed during quenching in polymer solutions. Fortunately, the report was saved and is now available for preparing a paper to be published in a scientific journal. For a long time, the data were put for conservation since a lack of suitable explanation and understanding process. Nowadays, many investigators observed the same strange effect and published their data [1-4]. Two hypotheses were forwarded to explain the strange behavior of surface thermocouples. One of them is a hypothesis on periodical change fast nucleate boiling process by slow cooling film boiling process resulting in “shoulder” formation [5]. Another hypothesis says that the reason for “shoulder” formation is the varying surface insulating layer [3, 4]. Nevertheless, there is a high time to come to a final conclusion what is the physics of the “shoulder” formation and how it can be used in practice. The aim of the current paper is to solve this important and very interesting problem.

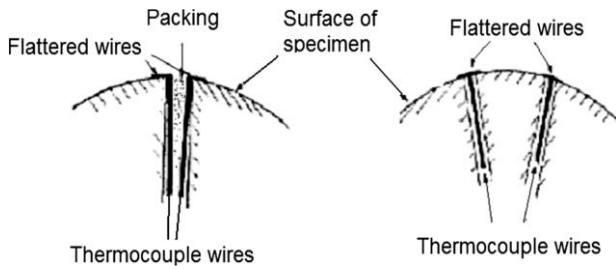
## II. THE PROBE INSTRUMENTATION

As known, it was developed the standard cylindrical probe 12.5 mm diameter with one thermocouple at its center for the testing cooling intensity of cooling media [6]. Unfortunately, the probe with one thermocouple located at its center cannot be used for the investigation of the self-

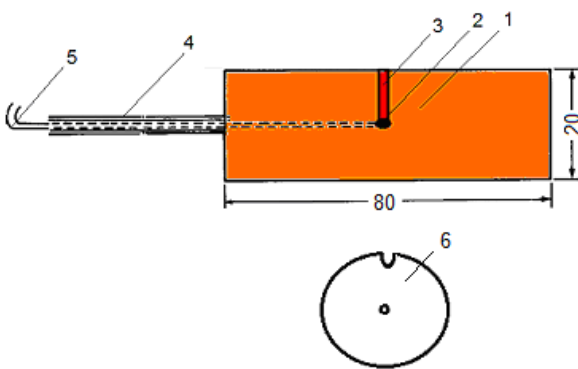
regulated thermal process, which is crucially important for science and for practice. That is why for the investigation of the self-regulated thermal processes and other “strange effects,” special instrumentation of thermocouples was performed. The technique of French [7] was used for flattening wires of a thermocouple which is shown in Fig. 1. The thin surface thermocouple tube was located in the keyway area, and thin wires 0.1 mm were flattened at the middle of the cylindrical probe. The central thermocouple was first welded in the center of the probe and then plugged with a pin made of AISI 304 steel. The surface of the cylindrical probe made of AISI 304 steel was polished to provide an ideal round surface (see Fig. 2). Prior to start tests, the probe was tested for repeatability and quality of flattening. Then both thermocouples were calibrated, and their cold ends were kept at a constant temperature to measure precisely surface temperature. Such measures are very important when investigating the transient nucleate boiling process where surface temperature changes insignificantly. Based on this accurate approach, the water polymer solutions of low concentration were carefully investigated.

The investigations were performed with a low concentration of the polyoxyethylene in cold water using a 20 mm cylindrical probe instrumented with two thermocouples, as discussed above. It was established that with the increased concentration of polyoxyethylene in cold water (beginning from 0.001 %), different heat transfer modes are observed, resulting in the elimination of film boiling process at 0.001 % concentration, increasing surface temperature of the probe during self – regulated thermal process by formation the “shoulder,” periodical changing of heat flux densities, slow cooling of surface temperature like in oil when the concentration reaches 1 % polyoxyethylene in water, and so on. It is underlined that low concentration of polyoxyethylene in water can serve as an excellent quenchant for accelerated and uniform cooling of steel parts quenching, by this way the cost of a coolant. In this case, accelerated cooling should be interrupted at the proper time to provide an optimal hardened layer after quenching. Such an approach guarantees increasing service life of steel parts after accelerated cooling with the significant decrease of their cost and eliminates carburization process; and the technology can be used for hardening large steel parts like large windmill gears, large bearing rings, etc.





**Fig. 1: Depiction of how thermocouples were arranged and accurately flattened to the wall of spheres and polished by French [7].**

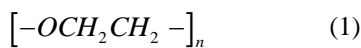


**Fig. 2: Instrumentation of thermocouples in the cylindrical specimen.**

Based on accurate instrumentation of the test probe, very interesting results of experiments were obtained, which are discussed below.

### III. RESULTS OF EXPERIMENTS

For the experiment, polymer polyoxyethylene was used. The chemical formula of polyoxyethylene is shown below [8]:

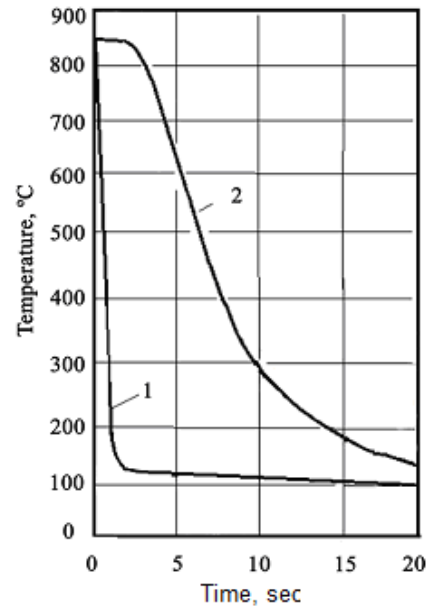


Number  $n$  in (1) is responsible for the molecule weight of polyoxyethylene. As known [8, 9], a very small amount of polyoxyethylene in water (0.001–0.003 %) decreases hydrodynamic resistance by 70 %. It is expected that the same amount of polyoxyethylene (POE) in water will affect its cooling intensity, too, eliminating the film boiling process. Note that intensive and uniform cooling increases the service life of hardened machine components and tools significantly.

The concentration of polyoxyethylene in water was 0.001 %, 0.01 %, 0.1 %, 0.2 %, 0.3 %, and 1 % [3].

As one can see from Fig. 3, film boiling during quenching in a low concentration of polyoxyethylene (0.001 %) at 23 °C is completely absent. The self-regulated thermal process lasts from 2 seconds to 15 seconds and cooling factor  $m$  during this period is equal to  $0.185 \text{ s}^{-1}$ , *i.e.*

$$m = \frac{\ln(700^\circ\text{C} - 100^\circ\text{C}) - \ln(205^\circ\text{C} - 100^\circ\text{C})}{13.7\text{s} - 4.3\text{s}} = 0.18543\text{s}^{-1}$$



**Fig. 3: Cooling curves versus time during quenching cylindrical probe 20 mm diameter and 80 mm long in a water solution of polyoxyethylene (0.001 %) at 23 °C: 1 is surface temperature; 2 is the core temperature**

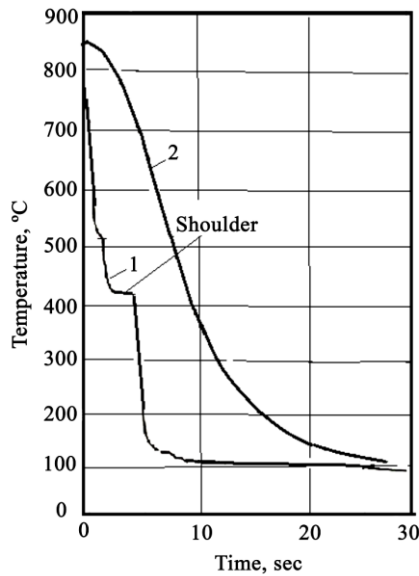
According to the second theorem of Kondrat'ev [8], the  $m_\infty$  is calculated as:  $m_\infty = \frac{a}{K} = \frac{4.95 \times 10^{-6} \text{ m}^2 / \text{s}}{17.29 \times 10^{-6} \text{ m}^2} = 0.2863\text{s}^{-1}$ , where  $K = R^2 / 5.783 = 17.29 \times 10^{-6} \text{ m}^2$ . Now, Kondrat'ev number is evaluated as  $Kn = \frac{0.1854\text{s}^{-1}}{0.2863^{2-1}} = 0.65$ . The

generalized Biot number  $Bi_v$  is evaluated from the universal correlation between  $Kn$  and  $Bi_v$  and is equal to  $Bi_v = 1.55$ . The number  $Kn$  is an average value. At the beginning of cooling, it is equal to 1, which looks like ideal cooling when  $Bi_v \rightarrow \infty$ . The average HTC during quenching in low concentration of polyoxyethylene (0.001 %) at 23 °C is equal to  $\alpha = \frac{20.25\text{W} / \text{mK} \times 1.55}{0.002162\text{m}} = 14518\text{W} / \text{m}^2 \text{K}$ . The surface

temperature of the probe drops from 850°C to 125°C within 1.25 s that coincides very well with experiments of French [7], who tested 5% water solutions of NaOH. It means that cooling in a low concentration of polyoxyethylene (0.001 %) at 23 °C is intensive and uniform and is similar to cooling in a 5% water solution of NaOH. Also, it coincides very well with the calculated data, namely with the initial temperature of the transient nucleate boiling process, which is calculated using equation regular thermal condition theory [10, 11]. According to [11], the initial temperature of the transient nucleate boiling process is 126°C, which perfectly coincides with our experiment.

Cooling curves versus time during quenching cylindrical probe 20 mm diameter and 80 mm long in a

water solution of polyoxyethylene (0.01 %) at 23°C are shown in Fig. 4.



**Fig. 4: Cooling curves versus time during quenching cylindrical probe 20 mm diameter and 80 mm long in a water solution of polyoxyethylene (0.01 %) at 23°C: 1 is surface temperature; 2 is the core temperature**

During quenching cylindrical probe 20 mm diameter and 80 mm long in a water solution of polyoxyethylene (0.01 %) at 23°C, a “shoulder” emerged on the surface cooling curve in the area 420°C which lasted a couple of seconds (see Fig. 4). At the beginning of the experiments, we followed an opinion that the experiment was wrong and something wrong was with the surface instrumented thermocouple. After controlling surface flatter and repeating experiments, it was clear that surface thermocouple showed correct results of measuring and “shoulder” on the surface cooling curve is a real phenomenon.

Using regular thermal condition theory, let’s calculate cooling factor  $m$  for the central cooling curve provided in Fig. 4:

$$m = \frac{\ln(700^\circ C - 100^\circ C) - \ln(205^\circ C - 100^\circ C)}{15s - 5s} = 0.1743s^{-1}$$

According to the second theorem of Kondrat’ev [10], the  $m_\infty$  is calculated as:

$$m_\infty = \frac{a}{K} = \frac{4.95 \times 10^{-6} m^2 / s}{17.29 \times 10^{-6} m^2} = 0.2863s^{-1}$$

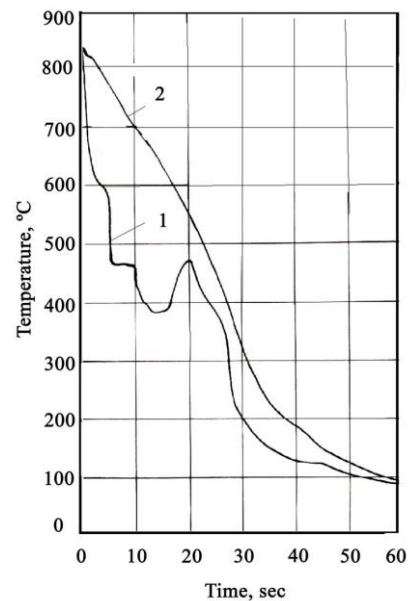
where  $K = R^2 / 5.783 = 17.29 \times 10^{-6} m^2$ . Now, Kondrat’ev number is evaluated as  $Kn = \frac{0.1743s^{-1}}{0.2863s^{-1}} = 0.609$ ;  $Bi_V = 1,30$ ;

$$\alpha = \frac{20.25W / mK \times 1.30}{0.002162m} = 12176W / m^2 K$$

As seen from Fig.4, a central thermocouple was not affected by the “shoulder” created by an insulating layer. It means that investigators who used probes with one thermocouple at the center of probes have lost a lot of important information, which could be depicted only by the accurately instrumented surface thermocouple.

Tests of water solution of polyoxyethylene (0.2 %) at 23 °C showed more unexpected results of measurements

(see Fig. 5). A “shoulder” in a given solution lasted almost 15 seconds, and a strange increasing surface temperature was observed during the experiment (Fig. 5). These experiments were carries out in Ukraine in 1983. They were not published for a long time due to very strange results of experiments and no explanation and understanding of the cooling process. These strange results of experiments were for the first time published in the journal “Eureka: Physics and Engineering” only in 2018 [3]. The observed phenomena are explained in the current paper-based on the existing the self-regulated thermal process and varying of the surface polymeric layer during quenching of probe.



**Fig. 5: Cooling curves versus time during quenching of cylindrical probe 20 mm in diameter and 80 mm long in a water solution of polyoxyethylene (0.2 %) at 23 °C: 1 is surface temperature; 2 is the core temperature**

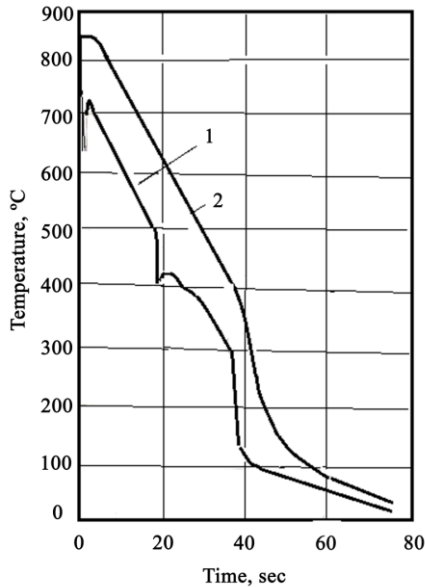
Further, increase polyoxyethylene to 0.3 % in water at 23 °C results in a periodical change of film boiling by the transient nucleate boiling process (see Fig. 6). Obtained results were used for the statistical method of solving an inverse problem which was published in 1994 [12]. According to the results of calculations, periodical change occurs in 18 seconds period and is explained by forming and dissolving of the polymeric layer that requires a relatively long time. So, one of the features of periodical change heat flux densities and HTC’s is its relatively long period connected with the formation and dissolving of the polymeric layer.

Increase concentration of polyoxyethylene to 1% in water at 23 °C results in developing a full film boiling process and slow cooling. The results of the test were published in 2018 [3].

More information on the chemical and physical properties of polyoxyethylene one can find in references [8, 9].

It should be noted here that the cooling intensity of water polymer solution along with concentration

depends on the length of the chain of the polymeric molecule; therefore, prior to starting preparing polymer water concentration, one should pay attention to the molecular weight of the polymer.



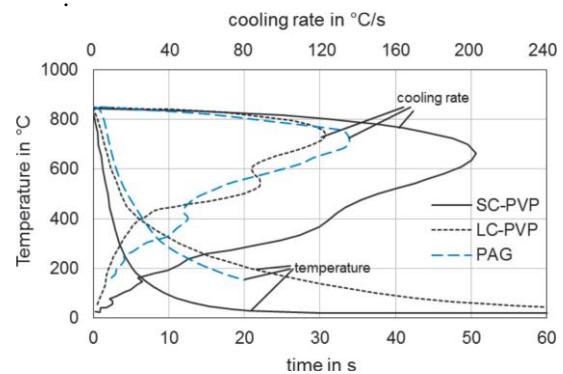
**Fig. 6: Cooling curves versus time during quenching cylindrical probe 20 mm diameter and 80 mm long in a water solution of polyoxyethylene (0.3 %) at 20 °C: 1 is surface temperature; 2 is the core temperature**

In 2019 in Germany were published very important and accurate investigations of authors [5] who investigated the cooling intensity of polyvinylpyrrolidone (PVP) and polyalkylene glycol (PAG) water solutions using standard Inconel 600 probe 12.5 mm diameter and large shaft 150 mm diameter and 580 mm length (78 kg mass). These experiments are really extremely important since for the first time were tested small and very large cylindrical samples which make a basis for the possibility of transition from data obtained by the small probe to data used for very large components.

Let's analyze accurate experimental data obtained in Germany by authors [5]. First of all, let see what cooling characteristics of SC-PVP and PAG water

solutions tested by standard probe 12.5 mm diameter (see Fig. 7) are).

For comparison was used the same methodic of Kn, and HTC evaluation was widely discussed above.



**Fig. 7: Temperature/cooling rate and temperature/time plots of IVF SmartQuench tests for the investigated polymers [5].**

As known, water solutions of polymers such as polyvinylpyrrolidone (PVP) and polyalkylene glycol (PAG) are used in the heat treating industry for immersion quenching because of their unique features and quenching characteristics [5]. To make recipe calculations possible, one needs accurate data on Kn and HTCs that are related to PVP and PAG solutions. Table 1 provides such data, which are based on accurate experiments presented by Fig. 7. As seen from Fig. 7, the film boiling process is completely absent from the very beginning of the standard cooling probe, and the maximal cooling rate is rather high (see Fig. 7). Knowing cooling rates vs. time Kn, Bi<sub>v</sub>, and HTCs were calculated (see Table 1). As compared with the cooling characteristics of 5% water NaOH solution, obtained data for PVP and PAG solutions are a little bit smaller due to the existing surface polymer insulating layer that decreases cooling rate during quenching. However, the surface insulating layer, along with the eliminating film boiling process, provides very uniform cooling and heals possible micro-quench cracks by covering the surface smoothly with a thin layer of polymer.

**TABLE I**  
Effect of the core temperature of smart probe on cooling rate v. Kondrat'ev numbers Kn, generalized Biot number Bi<sub>v</sub> and HTC for aqueous solution SC-PVP quenchant.

T, °C	200 °C	300 °C	400 °C	518 °C	600 °C	700 °C
v, °C/s	40	80	124.7	160	196	200
Kn	0.69	0.66	0.66	0.58	0.56	0.501
Bi <sub>v</sub>	1.85	1.60	1.60	1.15	1.10	0.88
HTC, W/m <sup>2</sup> K,	12920	11840	12530	9575	9590	8030

Table 1 shows that cooling in a water solution of polymers was close to intensive quench process, and film boiling was completely absent from the very beginning of immersing

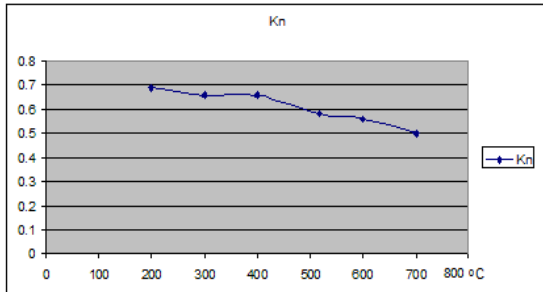
Fig. 8 and Fig. 9 show how dimensionless number Kn and HTCs change along with changing core temperature

of the probe. The value of Kn changed within 0.5 – 0.68 when core temperature changed from 200°C to 700°C. For cooling time calculations can be used, the average value of Kn is equal to 0.59. Knowing dimensionless number Kn, it is possible to calculate core temperature and cooling rate

for any size and form of steel part using the equation below:

$$v = \frac{aKn}{K}(T - T_m) \quad (2)$$

Here  $v$  is the cooling rate in  $^{\circ}\text{C/s}$ ;  $a$  is thermal diffusivity of material in  $\text{m}^2/\text{s}$ ;  $K$  is Kondrat'ev form coefficient  $\text{m}^2$ ;  $T_m$  is bath temperature  $^{\circ}\text{C}$ .



**Fig. 8: Dimensionless number Kn versus core temperature of the smart probe.**

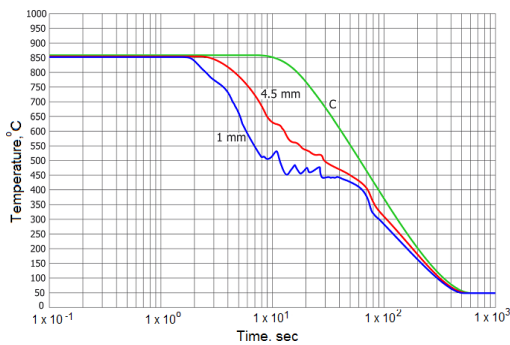
Results of current investigations can be used for core hardness and microstructure perdition when quenching in water polymer solutions [13]. The prediction is based on the use of equation (2), Jominy curves a Kondrat'ev numbers Kn (see Table 1 and Table 2) [13].

**TABLE II**

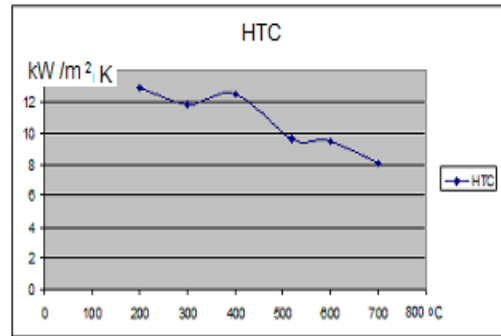
**Effect of the core temperature of the smart probe on cooling rate v. Kondrat'ev numbers Kn. Generalized Biot number Biv and HTC for aqueous solution Poly(Alkylene Glycol) Quenchant...**

T, °C	200°C	300°C	400°C	518°C	600°C	700°C
v, °C/s	28	28.5	53	60	100	136
Kn	0.190	0.235	0.28	0.282	0.294	0.341
Biv	0.222	0.286	0.36	0.365	0.385	0.48
HTC, W/m <sup>2</sup> K,	1550	2117	2814	2900	3357	4380

The most interesting result of the investigation performed in Ukraine, Croatia and Germany is a stable “shoulder” formation on the surface cooling curves during quenching. Liscic probe and large shaft 150 mm diameter, 580 mm length weighting 78 kg (see Fig. 10 and Fig. 11) [1, 2, 5] were used for testing PAG polymers which are widely used in the heat treating industry.



**Fig. 10: Cooling curves measured by the Liscic/Petrofer probe quenched in liquid media: (a) in accelerated mineral oil of 50°C, without agitation; (b) in a polymer solution of 35°C, with agitation [2].**

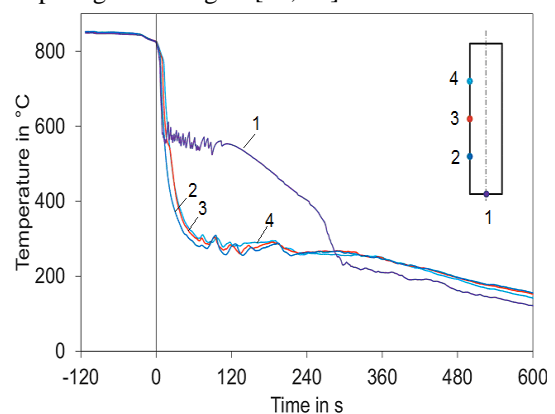


**Fig. 9: HTC versus core temperature of the smart probe.**

Increasing HTC with decreasing core temperature of smart probe is a piece of evidence that surface polymeric layer was decreased versus time resulting in the increasing heat flux density going from polymeric surface to liquid.

Similar calculations were fulfilled for water solutions of PAG polymer (see Table 2). Obtained results of calculations approach the cooling intensity of some fast cooling oils,

Fig. 10 and Fig. 11 show stable and repeatable “shoulder” formation that is important for developing novel austempering technologies [14, 15].



**Fig. 11: Cooling curves of a shaft (150 mm diameter, 580 mm long, and 78 kg mass) quenched in an industrial quench tank filled with 18% water solution of PAG solution. Colored spots indicate the measuring positions [5] schematically.**

#### IV. EXPLANATION OF STRANGE EFFECT

Now, when the self-regulated thermal process is enough investigated and effect of the surface insulating polymeric layer is established, it is possible to explain the nature of appearing a “shoulder” on the surface curves. Let’s start with the law of energy conservation consisting of equities of heat flux densities on the boundary metal – polymeric layer (see Fig. 56) that can be written as:

$$q_{ml} = q_{pl} \quad (3)$$

or

$$\lambda_{ml} gradT_{ml} = \lambda_{pl} gradT_{pl} \quad (4)$$

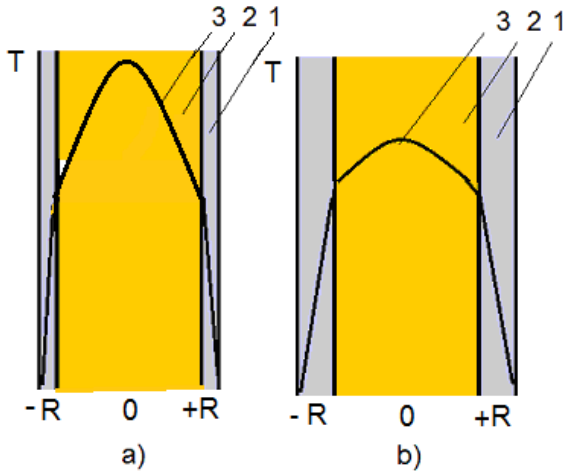
or

$$gradT_{ml} = \frac{\lambda_{pl}}{\lambda_{ml}} gradT_{pl} \quad (5)$$

Equation (5) along with equation (6) was used to explain the process of “shoulder” formation during quenching in polymers.

$$T_{sf} = T_s + \Delta \bar{\xi} \approx const \quad (6)$$

During immersion of the heated probe into the water polymer solution, the surface of the probe is immediately covered by a thin polymeric layer, which then increases with passing time (Fig. 12 a)). A scheme of Fig. 12 was built according to visual experiments of Tensi [15, 16].



**Fig.12: Explanation of a “shoulder” formation during quenching in polymer solutions.**

Because  $\frac{\lambda_{pl}}{\lambda_{ml}} \ll 1$  the temperature gradient in metal during cooling is low, while the temperature gradient in the polymeric layer is very large (see Fig. 12), it is because the thermal conductivity of the polymeric layer is known as 0.2 W/mK while the thermal conductivity of steel during quenching is approximately 23 W/mK. They can be different, but always the inequity  $\frac{\lambda_{pl}}{\lambda_{ml}} \ll 1$  will be true. It

means that the temperature gradient inside the metal is always much smaller as compared with the temperature gradient inside the polymeric layer. (Fig. 12).

According to accurate experiments of Tensi [14, 15], during immersion into the water polymer solution, the thin surface insulating layer appears immediately, which then quickly increases, creating the smaller temperature gradient inside the polymeric layer. Since during these self-regulating thermal process, the surface temperature on the insulated probe maintains relatively a long time at the level of the boiling point of a liquid, we can conclude that surface temperature is fixed (see Eg. (6)). It means that temperature on the metal surface will increase when the thickness of the insulating layer increases. The significant increase in surface temperature on Fig. 5 is explained by the quick increase of the insulating layer during the transient nucleate boiling process. Slow oscillation of metal surface temperature is explained by the varying thickness of the insulating layer. Moreover, since the insulating layer prevents the film boiling process, the hypothesis that “shoulder” is generated by periodic replacement of the nucleate boiling process with the film boiling is questionable [5].

The discovered stable delaying of metal surface cooling has a great future because a novel technology on performing austempering and martempering processes via cold liquids was proposed by the author [16]. The new technology saves energy and makes the environment green.

Unfortunately, manufacturers don’t pay enough attention to the physics of the boiling process in polymer solutions, and due to this fact, they don’t achieve a full benefit from selling their product.

#### V. CONCLUSIONS

1. The formation of the stable “shoulder” on surface cooling curves is explained by the existence of the self – regulated thermal process on the insulation and varying the thickness of the insulating layer during quenching in water polymer solutions.
2. The discovered effect can be successfully used for performing austempering processes via colds liquids resulting in huge benefits.
3. If further careful investigations in studying the physics of boiling processes during quenching in polymers solutions will make progress, the income of polymer manufacturers will increase due to opening new fields of polymers requirement.

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