Characteristic features of the cooling capacity of aqueous polymer solutions

T V Shveyova 1, G F Muhametzyanova 2, V I Astashchenko 2, N N Zapadnova 3 and E A Zapadnova 2

1 Branch of Kazan Federal University in Naberezhnye Chelny, Service of Transport Systems Department, Tatarstan Republic, Russia, 423812 Naberezhnye Chelny, Syuyumbike Avenue, 10A
2 Branch of Kazan Federal University in Naberezhnye Chelny, Department of Materials, Technologies and Quality, Tatarstan Republic, Russia, 423812 Naberezhnye Chelny, Syuyumbike Avenue, 10A
3 Technical College n.a. V.D. Potashov, Tatarstan Republic, Russia, 423827, Naberezhnye Chelny, Motornaya Str., 13A

Abstract. For the study of quenching medium a special sample is developed that provides high reproducibility of thermal processes occurring on the surface of the cooled product. The results of the cooling method of aqueous solutions with different polymer content are given. The application of thermogravimetric analysis for the study of physical and chemical processes occurring during heating of a synthetic quenching medium is considered. The temperature intervals of endo-exothermic reactions as a result of oxidation of the polymer component of the solution are shown. The reasons for the formation of two extrema on the cooling capacity curve of aqueous polymer solutions are indicated.

Thermal and surface deformation treatments are the key factors in the system of formation of the structure, properties and reliability of metal products in operation [1, 2]. The most difficult tasks in the field of heat treatment include issues related to the processes of quenching cooling of metal products. A key role in solving this problem is given to the quenching medium. Thanks to its competent and well-equipped application, it is possible not only to control the cooling process, and, therefore, the structure formation of steel during the heat treatment of metal products, but also to solve issues of environmental nature, the cost of production and technological safety. The analysis of literature and patent research indicate that the management of the hardening process is a very difficult task, but the effect of its competent solution is really high. It is known [3-6] that the quenching media must have a strictly defined cooling capacity in the specified temperature ranges of the quenched product, maintain their properties for a long period of operation, be environmentally safe, etc.

Quenching media based on water-soluble polymers, widely used since the middle of the XXth century are of particular interest, as they are devoid of drawbacks that exist in traditional quenching media such as water and oil. Depending on the content of the polymers in water, it is possible to change the cooling ability of the environment from the cooling rate in water to cooling rate in oil [4-11].

On the basis of the analytical review of information sources [3-12] it is established that for all synthetic media a certain pattern is clearly traced, expressed in the presence of two maxima on the dependence of their cooling capacity (Fig. 1). However, there is not enough available information about
the causes of high and low cooling rates inherent in them, and they do not give a clear answer to this question. Typically, these dependences are associated with the temperature intervals of the boiling point of the quenching fluid that can be changed by hardening in media under pressure [12] or by introducing various additives [8 - 11]. Due to these additives, the temperature range of the film and bubble boiling is changed and, accordingly, an indispensable cooling rate is achieved in a given temperature range.

![Fig. 1 – Cooling capacity of aqueous solutions "Osmanil-E2 "(1)," PK – 2 "(2)," Tosol – K "(3,4) and" Kamgidrol-ZAK " (5) at different polymer content (wt. %): 1 – 6%; 2 - 0,65%; 3 – 32,5%; 4 – 50%; 5 - 18%.](image)

It should be noted that such additives themselves in high temperatures during quench cooling of the metal are able to undergo a physical-to-chemical reactions: decomposition, oxidation, destruction, melting, recovery etc. When dipping the hot product into the quenching medium at the interface "metal-liquid", these endo-exo-effects create a thermal effect on the surface. The temperature gradient between the surface of the product and the liquid is determined by the amount of heat that is released or absorbed as a result of such reactions. Depending on the type and concentration of the additive in the liquid medium, the level of the thermal effect also changes. Finding out the reasons for the low and high cooling rates on the dependence \( V_{\text{cool}} = f (T \, ^\circ C) \) and establishing the ability to control these values is an important task for specialists engaged in heat treatment of metal products.

**Purpose of Work.**

Study of the cooling capacity of aqueous polymer solutions and justification of the extreme values of the cooling rate at this dependence.

**Materials, Research Methods and Results.**

To achieve this goal, the paper has investigated aqueous solutions of liquid "TOSOL-K" [9, 10], which are most often used for bulk and surface hardening of parts. "TOSOL-K" is a concentrated liquid, which contains ~50% of the polymer with the presence of anti-corrosion, anti-foaming and stabilizing additives. Polyglycol – nonylphenol ethoxylates is used as the polymer, and the sodium nitrite and triethanolamine are used as corrosion additives. To ensure the manufacturability of the environment during operation and storage in its composition there are silicone defoamer, castor oil and potassium benzoic acid in small quantities. The study was subjected to aqueous solutions of liquid "TO-
SOL-K”, in which the polymer content was 5%, 15% and 32.5%, as well as 50% (liquid concentrate). The polymer content in the solution was determined by density. The cooling capacity of quenching solutions [12] was estimated by temperature regulation of the inner surface of a specially designed copper sample with a wall thickness of 1.7 mm (Fig. 2A). Thermal calculations have found that the temperature difference between the outer surface of the cooled sample and the controlled area at a specified distance from the surface does not exceed 11°C.

Using the proposed design of the sample, a high reproducibility of the processes occurring on the surface was achieved and, accordingly, it is possible to constant the accuracy of determining the cooling capacity of liquid media. The results of the study of aqueous polymer solutions of different concentrations has shown that with an increase in the content of nonylphenol ethoxylates in water, the cooling capacity decreases (Fig. 2 b). Thus, an increase in its content in the solution from 5 to 50% reduces the cooling capacity of the quenching medium in the perlite transformation temperature range from 300-320°C/s to 70-75°C/s, and in the martensitic transformation temperature range – from 400°C/s to 80°C/s. It is noteworthy that there are two maxima on the curves of \( V_{\text{cool}} = f (T \degree C) \): one in the range of 600-680°C, the second – at 280-300°C. The answer to the reason of formation of two peaks on the curve is performed on the thermogravimetric analyzer TG209F1/is/ (f. Netzsch, Germany). Using this method, information on the behavior of the quenching liquid "TOSOL-K", containing 50% of the polymer, when heated from 20 to 800°C was got (Fig. 3).

As a result of the study, the dependence of the mass change on the heating temperature (HT), the change in the rate of mass loss on the temperature (DT), and the curves of temperature change (T) and its differential version (DCT) are obtained. Special attention should be paid to the dependence of DCT, which characterizes the endo-exothermic reactions occurring when the quenching medium is
heated. It is established that in aqueous solution based on the studied polymer, there are two effects: endothermic – in the temperature range 110 - 170°C and an exothermic asymmetric – in the range of parator 280 - 510°C. It was found that the endothermic peak is associated with boiling water, and its end at 170°C corresponds to the lower boiling crisis – the minimum temperature of stable bubble boiling. The specified temperature determined by the method of dripping [13] corresponds to 157°C [14].

The exothermic peak with a maximum at 400 °C is associated with intensive oxidation of the polymer component under the influence of temperature and sodium nitrite, the decomposition of which is known to occur at 380°C. Comparison of the cooling curves and the differential curve of the temperature change (DCT) of the aqueous solution with the content of nonylphenol ethoxylates shows that the decrease in the cooling capacity in the temperature range of 300-600°C is associated with the exothermic effect arising during the oxidation of the polymer component of the quenching medium (Fig. 3). On the DCT curve, the maximum of this effect corresponds to 400°C, which is explained by a decrease to a minimum value of the cooling rate at a temperature of 400°C (Fig. 2, Fig. 4).

Thus, as a result of thermogravimetical analysis of polymer quenching media, it can be stated that due to the exothermic reaction, accompanied by heat generation, two bright peaks were formed on the curve of cooling rate – one of which is at the temperature of the beginning of this reaction and the second one – at a temperature of completion of the reaction.

**Conclusion**

1. An effective method for determining the cooling capacity of quenching media has been developed and tested. It is established that the cooling rate of the solutions decreases with increasing content of nonylphenol ethoxylates in the water.

2. The possibilities of thermogravimetical method for the study of quenching media based on water-soluble polymers are shown. The technique allows to register physical and chemical processes occurring during heating of quenching liquids and establish endo-exothermic effects and temperature intervals of these reactions.

3. On the cooling rate curve of aqueous solutions "TOSOL-K" two extreme values were revealed – at 600°C and 300°C, which are formed as a result of polymer oxidation at high temperature quenching medium. This reaction is observed in the range of 500-300°C and is accompanied by an exothermic effect with a maximum heat release at 400°C. The beginning and the completion of the exo-reaction correspond to the maxima of the cooling rate of the quenching liquid under study.
Fig. 3. - Thermographical scheme of liquid concentrate "TOSOL-K": T – temperature change in time; HT – dependence of mass change of the body temperature; DT – dependence of the rate of mass loss of temperature; DCT – differential curve of the temperature change.

Fig. 4. - The influence of the exothermic effect during the heating of the quenching medium on the cooling ability of the concentrate "TOSOL-K".

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