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RESEARCH ARTICLE

PECULARITIES OF QUENCHING PROCESSES IN PIB SOLUTIONS OF SOYBEAN OIL

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ABSTRACT

The paper discusses the results of investigations connected with the cooling characteristics of pure soybean oil and its PIB solutions of different concentrations. In contrast to mineral oils, in vegetable oils film boiling in many cases is absent due to formation of an insulating surface layer which decreases initial heat flux density. In the paper is shown that initial heat flux density can be decreased for 50% and can be less than the first critical heat flux. It means that nucleate boiling process starts immediately after immersion of probe into oil and additives affect insignificantly cooling processes during nucleate boiling stage. In soybean oil additives affect significantly convection due to increasing viscosity. Vegetable oils are promising as the suitable quenchants when protected from oxidation and optimized within the boiling and convection modes.

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INTRODUCTION

In previously published papers (Kobasko, 2012; Lohvynenko *et al*., 2016; Kobasko *et al*., 2016), it was shown that small additions of polyisobutelene (PIB) to mineral oils radically change their cooling capacity through the elimination of film boiling process. Two hypotheses have been put forward to justify this phenomenon. PIB molecules accelerate the vaporization (evaporation) in quenching oil and the vapor pressure is achieved faster and as a result the vapor breakthrough the oil boundary which comes into contact with the heated metal surface and the nucleate boiling starts (Petrash, 1959). However, according to (Малиновский, 1993) PIB additives in the coolant oil for metal machining significantly reduces evaporation at a temperature 700°C - 800°C which contradicts the initial assumption that the PIB accelerates the process of vaporization. According to (Petrash, 1959), the PIB molecules shift the equilibrium

$$\text{Evaporation} \quad \underset{\longleftarrow}{\overset{\text{PIB}}{\longrightarrow}} \quad \text{Condensation}$$

to the right*; i.e*. PIB molecules are centers of condensation, whereby the existence of vapor is reduced. This mechanism is consistent with the results of studies (Малиновский, 1993).

The author (Kobasko, 2012) has a different opinion. He has made specific calculations showing the role of thermal insulation coatings, formed during the quenching process, on the value of heat flux density. It is well known that in vegetable oils the vapor film is absent without any additions of PIB to them. This is easily explained by the decomposition of the vegetable oil to form insulating layer on the metal surface which decreases initial heat flux density and prevents film boiling. The initial heat flux density depends on the thickness of the insulating layer and its thermal conductivity and is calculated by the equation (Kobasko, 2012):

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$$q_t = \frac{q_0}{1 + 2\dfrac{\delta}{R}\dfrac{\lambda}{\lambda_{coat}}} = \frac{q_0}{n}, \qquad (1)$$

$$\delta << R$$

where one can calculate the number n from the equation (1) as:

$$n = 1 + 2\frac{\delta}{R}\frac{\lambda}{\lambda_{coat}} \qquad (2)$$

According to the author studies (Kobasko, 1980), the first critical heat fluxes of oils are in the range of 2 - 3 MW /m^2. Assume that the first critical heat flux density of soybean oil is 2 MW/m^2. The thickness of insulating layer is 25 microns. The thermal conductivity of insulating layer is equal to 0.4 W/m K (Richter *et al*., 1984). It is required to determine how many times the insulating layer decreases the initial heat flux if it was 2.2 MW/m^2 initially. One can calculate n from equation (2), *i.e.*

$$n = 1 + 2\frac{25\times10^{-6}\,m}{5\times10^{-3}\,m}\frac{20W/mK}{0.4W/mK} = 1.5\,.$$

The above calculation shows that the initial heat flux density which was 2.2 MW/m^2 is reduced by half when insulating layer exists, *i.e.* it becomes equal to 1.46 MW /m^2 that is below the critical value. Therefore, there is no film boiling. Evidences are also experimental data on tests of soybean oil discussed below.

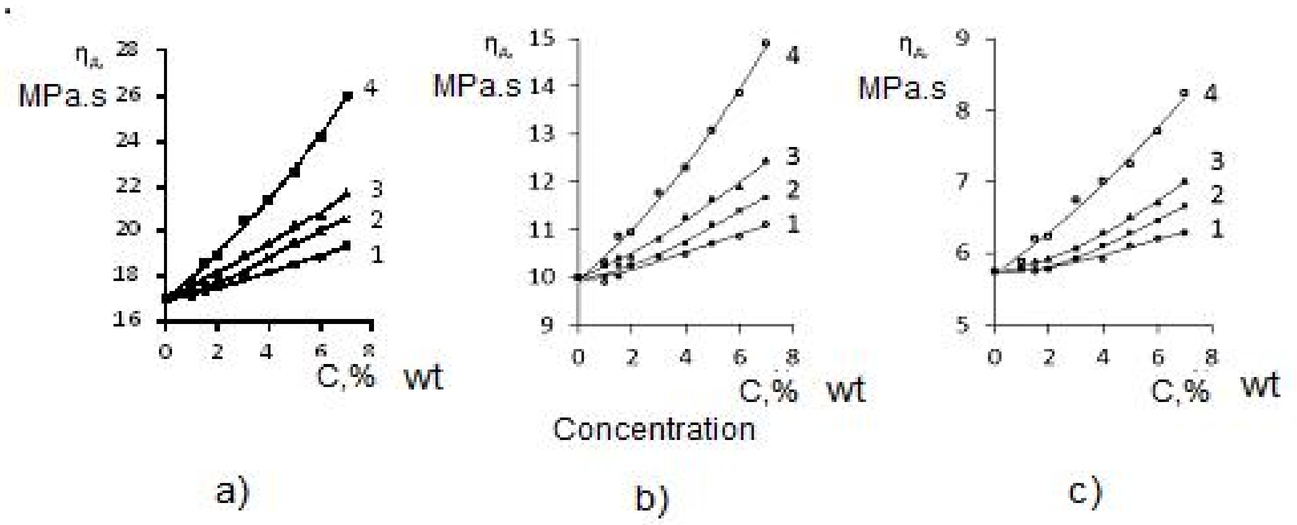

Fig. 1 Viscosity (η_D) versus concentration of PIB (Mw) and temperature: 1 – 680; 2 – 950; 3 – 1300; 4 – 2400 a) - 50°C; b) - 70°C; c) - 95°C (Dr = 729c^{-1})

The cooling properties of a soybean oil and PIB solutions

Analysis of the literature shows (Souza *et al*., 2014; Andrio *et al*., 2012; Totten *et al*., 1999; Кобаско, 1976; Canale *et al*., 2005) that in terms of production and a set of chemical and physical parameters the greatest potential for widespread industrial use has soybean oil if its thermo-oxidative stability is improved by antioxidant additives (Малиновский *et al*., 1993; Souza *et al*., 2014). According to the results of our preliminary research, the rheological properties of the soybean oils can be controlled by the small additions of viscosity index improver - polyisobutylene (PIB) which depends on the molecular weight (Mw) and may be a oligomer (Mw ≤ 5 · 10$^{4)}$, or polymer (Mw ≥ 5 · 10$^{4)}$ (Сангалов and Минскер, 2001). According to the results of preliminary experiments, the solubility of the PIB with Mw ≥ 5 · 10^4 in soybean oil significantly decreases. Therefore, as a viscosity index improver PIB oligomers with Mw = 680 (PIB 680) have been selected: 950 (PIB 950); 1300 (PIB 1300), and 2400 (2400 PIB). Studies rheology oligomer solution in soybean oil were made by rotational viscometer Reotest -2 instrument with digital display of the results in a wide range of concentrations of oligomers. The results are shown in Fig.1.

As seen from the results shown in Figure 1, the content of oligomeric PIB in soybean oil can significantly expand the range of values η_D in the temperature range 50°C - 95°C. These options are implemented in the quench tanks in a production environment. However, the viscosity doesn't have an impact on the processes of boiling (see Table 1 - Table 4). Increased viscosity significantly affects the convective heat transfer slowing the cooling rate in the martensitic range. This is a very positive factor. Methods of measurement and processing of the experimental data are presented in publications (International Standart ISO 9950; Москаленко *et al*., 2011). The results of studies of the concentration dependence of the cooling process of the thermal probe in soybean oil and oligomeric solutions are presented in Tables 1-4.

Comparative analysis of the concentration dependences of rheological properties of PIB solution in soybean oil (see Table 1 - 4) showed insignificant change (not more than 11.3 percent) of all the parameters during boiling process.

Table 1. Cooling curves analysis data vs. concentration of PIB 680 in soybean oil at 70°C

Symbols	Concentration of PIB , % wt.								
	0.0	1.0	1.5	2.0	3.0	4.0	5.0	6.0	7.0
τ_{600}, s	3.8	3.7	3.7	3.9	3.9	4.0	4.1	4.0	4.0
τ_{400}, s	8.0	8.0	8.2	8.4	8.5	9.4	9.1	8.8	8.8
τ_{200}, s	31.5	30.1	30.7	31.3	31.3	33.4	33.7	33.4	33.1
V_t^{max}, °C/c	99.1	97.5	97.0	100.0	98.7	94.9	91.0	95.5	95.2
$T_3^{Vt\ max}$, °C	706	716	716	674	703	686	672	688	698
V_t^{300}, °C/c	9.2	9.8	9.7	9.4	9.4	8.8	8.7	8.4	8.6

Table 2. Cooling curves analysis data vs. concentration of PIB 950 in soybean oil at 70°C

Symbols	**Concentration of PIB , % wt.**								
	0.0	1.0	1.5	2.0	3.0	4.0	5.0	6.0	7.0
τ_{600}, s	3.8	4.2	4.1	4.3	3.5	4.0	4.1	4.3	4.1
τ_{400}, s	8.0	8.7	8.3	8.8	8.0	8.1	8.4	7.7	8.2
τ_{200}, s	31.4	32.1	31.3	32.4	31.7	31.9	32.6	28.1	32.2
V_t^{max}, °C/s	99.1	87.9	89.9	88.4	94.2	93.6	87.3	90.0	89.5
$T_3^{Vt\ max}$, °C	706	674	693	716	670	707	732	725	723
V_t^{300}, °C/s	9.2	8.9	9.6	8.7	9.1	9.1	8.6	13.6	8.7

Table 3. Cooling curves analysis data vs. concentration of PIB 1300 in soybean oil at 70°C

Symbols	Concentration of PIB , % wt..								
	0.0	1.0	1.5	2.0	3.0	4.0	5.0	6.0	7.0
τ_{600}, s	3.8	3.4	3.4	3.4	3.4	3.4	3.4	3.3	3.4
τ_{400}, s	8.0	8.0	7.4	7.5	7.7	7.8	7.8	8.0	8.1
τ_{200}, s	31.4	33.1	31.4	31.2	32.2	32.8	32.2	33.2	33.5
V_t^{max}, °C/s	99.1	102.8	111.7	109.1	111.7	106.8	111.4	110.1	112.4
$T_3^{Vt\ max}$, °C	706	705	691	712	705	681	696	713	699
V_t^{300}, °C/s	9.2	9.2	8.7	8.6	8.6	8.5	8.3	8.2	8.5

Table 4. Cooling curves analysis data vs. concentration of PIB 2400 in soybean oil at 70°C

Symbols	**Concentration of PIB , % wt.**								
	0.0	1.0	1.5	2.0	3.0	4.0	5.0	6.0	7.0
τ_{600}, s	3.8	3.7	3.8	3.7	3.8	4.0	4.0	4.0	4.1
τ_{400}, s	8.0	7.6	8.8	10.4	10.1	9.6	9.6	10.2	11.0
τ_{200}, s	31.4	31.7	33.4	36.1	35.2	35.0	35.2	36.3	37.4
V_t^{max}, °C/s	99.1	101.8	97.6	91.7	93.0	90.8	91.4	92.1	85.0
$T_3^{Vt\ max}$, °C	706	690	716	732	690	706	696	704	731
V_t^{300}, °C/s	9.2	9.0	8.6	8.3	8.8	8.4	8.6	8.5	8.5

Table 5. Physical properties and cooling curves analysis data depending on concentration of PIB in soybean oil

№ Blosks	**Physical properties of PIB**			**Cooling curves analysis at T_{oil} = 70°C**					
	C, %	Mw	$\eta_Д^{70}$, MPa·s	τ_{600}, s	τ_{400}, s	τ_{200}, s	V_t^{max}, °C/s	$T_3^{Vt\ max}$, °C	V_t^{300}, °C/s
1	0.0(CM)	820	10.00	3.8	8.0	31.4	99.1	706	9.2
	1.5	2400	10.84	3.8	8.8	33.4	97.6	716	8.6
	3.0	1300	10.80	3.4	7.7	32.2	111.7	705	8.6
	4.0	950	10.93	4.0	8.1	31.9	93.6	707	9.1
	6.0	680	10.84	4.0	8.8	33.4	95.5	688	8.4
2	3.0	2400	11.75	3.8	10.1	35.2	93.0	690	8.8
	5.0	1300	11.62	3.4	7.8	32.2	111.4	696	8.3
	7.0	950	11.66	4.1	8.2	32.2	89.5	723	8.7

The reason for such behavior of vegetable oils is the formation of insulating layer that eliminates full film boiling without additives of PIB. The proof is video observation presented in Fig. 2. It should be noted that under identical η_D^{70} PIB 1300 solution concentration values 7% by weight. and PIB 2400 Occupational 4% by weight. (Figure 1) cooling characteristics are significantly different. Especially value V_t^{max} which difference is 21.6°C/sec (Table 3 and Table 4). These results suggest that the kinetics and mechanism of boiling quench media based oligomers solutions in vegetable oil is defined as the rheological properties of the quenching medium and Mm oligomers. This is supported by the results of studies of the effect of concentration of oligomers and Mm different PIB mm cooling properties of oligomeric solutions presented in Fig. 3, Fig. 4 and Table 5. A comparison of the values of the standard indicators of the cooling process is done with a sample η_D^{70}= (10,85 ± 0,05) MPa · s (Table 5, part 1) and η_D^{70} = (11.65 ± 0,05) MPa · s (Table 5, block 2).

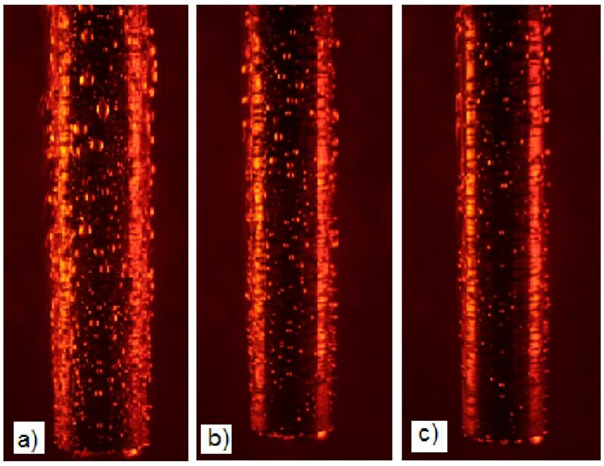

Fig. 2. Nucleate boiling process during quenching the probe in a pure soybean oil: a) at the beginning of cooling; b) at the middle of boiling process; c) at the end of nucleate boiling process

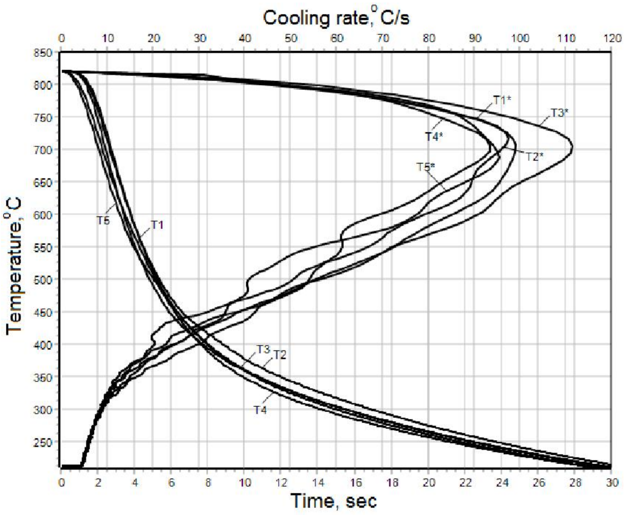

Fig. 3. Temperature vs. time and cooling rate vs. core temperature of cylindrical probe (D/H = 10/30 mm) when quenching in PIB solutions in soybean oil at 70°C : PIB 2400, C= 1.5% wt (T2); PIB 1300, C= 3% wt (T3); PIB 950, C= 4% wt (T4) ; PIB 680, C= 6 .0 wt (T5)

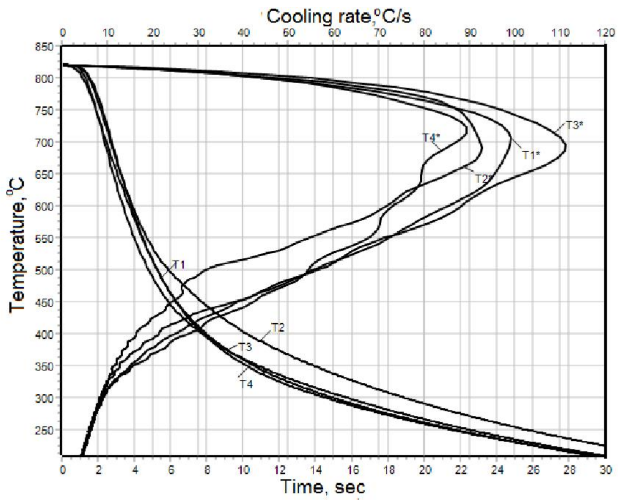

Fig. 4. Temperature vs. time and cooling rate vs. core temperature of cylindrical probe (D/H = 10/30 mm) when quenching in PIB solutions in soybean oil at 70°C : PIB 2400, C = 3 % wt (T2); PIB 1300, C= 5% wt (T3); PIB 950, C= 7% wt (T4)

As seen from Table 5, the value $\eta_Д$ for all four oligomeric solutions, having different values of V_t^{max}, is the same. According to (Ткачук *et al*., 1986), one of the quality criteria of quenching oils is its wettability which significantly affects the growth and separation of bubbles. In this regard, studies have been conducted to measure accurately γ depending on concentration of PIB using a modified Wilhelmy plate method (Файнерман *et al*., 1970). The results of measurements are shown in Fig. 5.

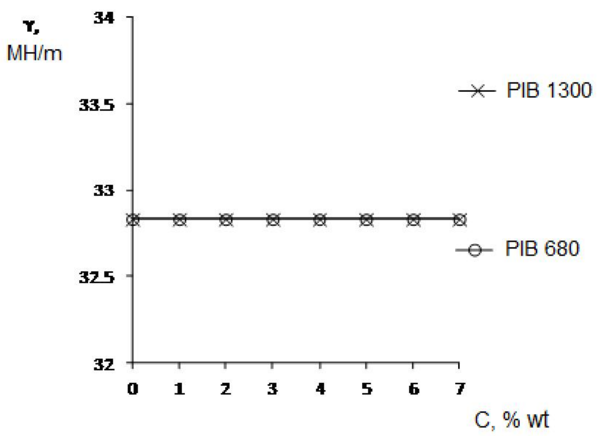

Fig. 5. Surface tension γ versus concentration of PIB in soybean oil at 20°C: PIB 680 (1); PIB 1300 (2)

As seen from Fig. 5, concentration of PIB 1300 and PIB 680 doesn't affect the value of γ while values V_t^{max} and $T_3^{Vt\ max}$ are slightly change that is shown in Table 5.

DISCUSSION

The aim of this paper is to show that vegetable oils can boil and absence of film boiling in them is explained by creation insulating layer that decreases initial heat flux density which becomes less than critical one that is why no film boiling at all. Actually, insulating layer is a product of interactions thermal and mechanical processes and transformation of soybean oil and PIB catalyzed by the metal surface. Probably, addition of PIB affects the composition of the insulating layer that in its turn affects cooling characteristics. Authors tested a small cylindrical specimen 10 mm in diameter and 30 mm long made of Inconel 600 material to produce high heat flux densities. In this case nucleate boiling process during quenching was clearly observed (Fig. 2). However film boiling was absent. It was an opinion that vegetable oils don't boil due to very large molecular and only convection phase takes place during quenching process.

Also, authors don't consider characteristics of cooling curves as the standard values. They are used only for comparison purposes. In practice, for investigations should be used larger probes like Liscic probe with instrumented thermocouples at the surface to solve correctly inverse problem (IP). The obtained results of investigations brought useful information when explore vegetable oils as the quenchants. For example, it is established that with increase concentration of PIB in soybean oil surface tension doesn't change. It means that additives of PIB cannot affect nucleate boiling processes which are function of surface tension value. Additives of PIB affect significantly convection which affects slightly transient nucleate boiling process. Results of investigations can be used by engineers dealing with heat treating processes. The soybean oil as a quenchant provides beneficial accelerated cooling rate within the nucleate boiling process and low cooling rate during convection. That is why the soybean oil is a perfect quenchant when oxidation processes in it are stabilized.

Conclusion

1. In contrast to mineral oils, during quenching in soybean oil full film boiling is completely absent due to formation of thin heat-insulating coating layer caused by the decomposition of vegetable oil.
2. Since the film boiling initially is absent, during quenching in soybean oil, additives of PIB insignificantly (not more than 11.3 percent) affect of its cooling properties.
3. The PIB oligomers in soybean oil considerably increase the viscosity, but virtually no effect on the wettability of the oligomer solutions.
4. It has been established that there is an optimal Mw of oligomer PIB at which effect of small additives on the process of cooling is realized the most clearly. It can be explained by optimal correlation between geometrical parameters of molecular PIB 1300 and soybean oil.
5. The key parameter that determines the efficiency of the effect of oligomeric additive on the values of cooling curves characteristics is absence of insulating layer on metallic probe
6. A concept, proposed by the author (1), on the surface insulating layer is very promising in terms of reducing the distortion of steel parts after quenching.
7. Slow cooling rate in the convective cooling region in soybean oil, caused by PIB additives, can reduce distortion.
8. Soybean oil for industrial purposes can be produced in less environmentally friendly areas that are an additional source of saving energy and materials.

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List of symbols

q_t is the heat flux density during cooling with a heat-insulating coating;

q_0, is the heat flux density without coating;

δ is thickness of insulating layer;

R is half of the specimen thickness,

λ is the thermal conductivity of the sample material,

λ_{coat} is the thermal conductivity of the heat insulating layer.

C, % is concentration of PIB

τ_{600}, s is cooling time from 825°C to600°C in s

τ_{400}, s is cooling time from 825°C to 400°C in s

τ_{200}, s is cooling time from 825°C to 200°C in s

V_t^{max} is maximal cooling rate in °C/s

$T_з^{Vt\,max}$ is core temperature of probe at the maximum cooling rate in °C

V_t^{300} is cooling rate when core temperature of probe is 300°C in °C/s

$\eta_Д^{70}$ is dynamic (shear) viscosity when liquid temperature is 70°C., MPa·s

Mw is molecular weight.

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