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**The regularities of glycerin trinitrate transition from the ballistic material to the water environment contacting with it**

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**Abstract**

In this paper the results of research concerning extraction process of trinitrate glycerin (TG) ballistite material in the aquatic environment are presented. Kinetic dependencies of changing of TG concentration in the aquatic environment of the various process parameters are presented. Based on these studies, formula for calculation of current value of the concentration of TG in the water is given.

Keywords: AQUATIC ENVIRONMENT, TRINITRATE GLYCERIN, EXTRACTION, BALLISTITE MATERIAL, KINETIC CURVES, PLASTICIZER

In the production, as well as while the disposal of such polymeric materials, such as ballistic powder and solid rocket fuel, these materials come into the contact with water [1, 2]. This leads to the transition of some trinitrate

glycerin (TG) which is a plasticizer of cellulose nitrate basics of the ballistic material in the aquatic environment. The resulting waste water, which is dangerous for environment, should be cleaned. For the rational organization of the process operation

there occurs the need of TG content predictive calculations, which depends on the specific transition conditions.

In essence, such transition is similar to the process of plasticizers solvents extraction. Well-known studies in this direction are connected with the definition of PVC plastics resistance to gasoline and other hydrocarbon environments, as well as plasticizers migration into the food from the plastic packaging [3,4]. They show that the plasticizer extractability depends on many factors: the type and amount of plasticizer, polymer characteristics, process conditions, solvent nature. However, in these studies, the solvents, generally well dissolve the plasticizer and the process is mainly determined by the phenomena occurring inside the solid phase (the solvent penetration to the primary matrix, disruption of intermolecular bonds of the plasticizer with the polymer, diffusion in the polymer).

The peculiarity of the water interaction with the ballistic material is that water has no affinity for the cellulose nitrate (the Hildebrandt solubility parameter of water is  $46.4 \text{ (MJ/m}^3)^{0.5}$ , cellulose nitrate –  $22.0 \text{ (MJ/m}^3)^{0.5}$ ). Accordingly, it cannot violate the coupling of TG with the cellulose nitrate. TG is also very limited dissolved by it ( $0.138 \text{ g/cm}^3$  at  $t=20^\circ\text{C}$ ). At the same time it is known that water environment, which contacts with the ballistic material, is characterized by the presence of TG [2].

In the view of the theoretical analysis complexity of TG transition from the ballistic material into the aquatic environment, the regularities of the process in this work were set according to the experimental studies basis.

The studies were performed in the laboratory conditions in the heated mixer with the volume of  $1.0 \text{ dm}^3$  with the propeller stirrer. The mixer was filled with water, and then the ballistic material was loaded and mixed with the agitator rotation frequency of 90 r.p.m. within a specified time. The ballistic material had the view of the plate with the size  $0.7 \times 10 \times 7.5 \text{ mm}$  and contained 40% (mass) of TG. At the end of each research the aquatic environment was separated from the material and the concentration of TG in it was measured with the spectrophotometric method (spectrophotometer UNICO2100). The results were presented as the graphs of concentration dependences according to the time for different process conditions.

The figure 1 shows the kinetic curves of TG concentration changes in the aquatic environment for the different mass values of the

ballistic material loaded into the mixer, which defines the number of TG entering into the system (Fig. 1a), the water environment volume (Fig. 1b) and its temperatures (Fig. 1c). This data shows that with the increase in number of TG  $G_0$ , which is entered with the ballistic material, the process temperature  $t$  and the water environment volume  $V$  reduction, the transition speed and TG concentration in it increase. At sufficiently large time consuming process the aqueous solution of TG approaches to the saturated state according TG and TG transition practically stops.

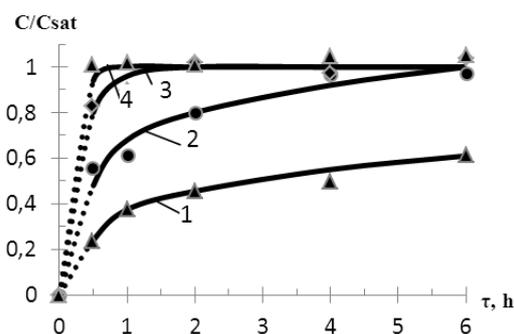


Fig. 1a

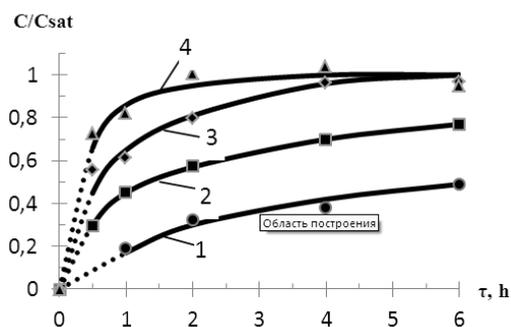


Fig. 1b

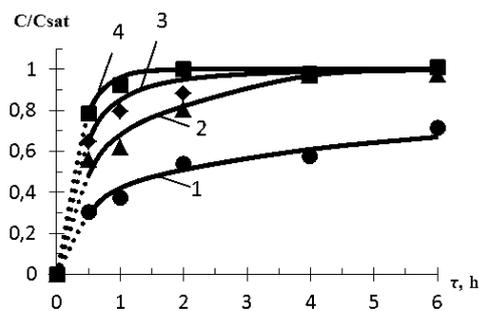
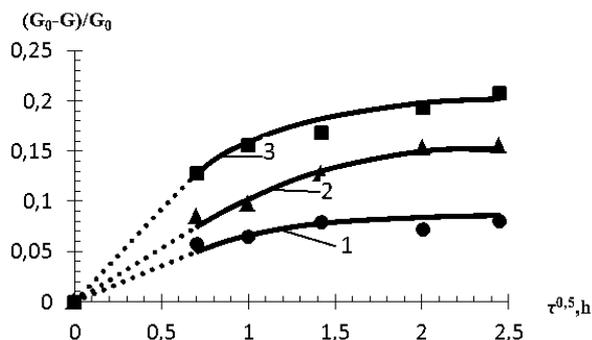


Fig. 1c

**Figure 1.** Kinetic curves of TG concentration changes in the aquatic environment under different process parameters: a - loading of the ballistic material: (1 -  $m_{load}=1,0 \cdot 10^{-3}$  kg, 2 -  $m_{load}=2,5 \cdot 10^{-3}$  kg, 3 -  $m_{load}=5,0 \cdot 10^{-3}$  kg, 4 -  $m_{load}=10,0 \cdot 10^{-3}$  kg); b - the water environment volume: (1 -  $V=0,4 \cdot 10^{-3}$  m<sup>3</sup>, 2 -  $V=0,2 \cdot 10^{-3}$  m<sup>3</sup>, 3 -  $V=0,1 \cdot 10^{-3}$  m<sup>3</sup>, 4 -  $V=0,05 \cdot 10^{-3}$  m<sup>3</sup>); c - the temperature: (1 -  $t=20$  °C, 2 -  $t=35$  °C, 3 -  $t=50$  °C, 4 -  $t=65$  °C)

The representation of the kinetic dependencies of ballistic material loss of TG in the coordinates  $G_0-G/G_0-\tau^{0.5}$  (Fig. 2), where  $G$  is the number of TG fallen into the aquatic environment during the time  $\tau$ , indicates these dependencies to be nonlinearity. This proves that in contrast to the plasticizers transition in other systems, for example, the migration in the aquatic environment of dioctylphthalate from the polymeric material such as artificial skin [5], in this case, the transition process is not limited by TG diffusion in the ballistic material. This can be explained by the high degree of plasticization of the original ballistic material.



**Figure 2.** Kinetic TG losses dependencies in the ballistic material under different process conditions: 1 -  $t=35$  °C,  $G_0=1,0 \cdot 10^{-3}$  kg,  $V=0,05 \cdot 10^{-3}$  kg; 2 -  $t=35$  °C,  $G_0=1,0 \cdot 10^{-3}$  kg,  $V=0,1 \cdot 10^{-3}$  kg; 3 -  $t=50$  °C,  $G_0=1,0 \cdot 10^{-3}$  kg,  $V=0,1 \cdot 10^{-3}$  kg.

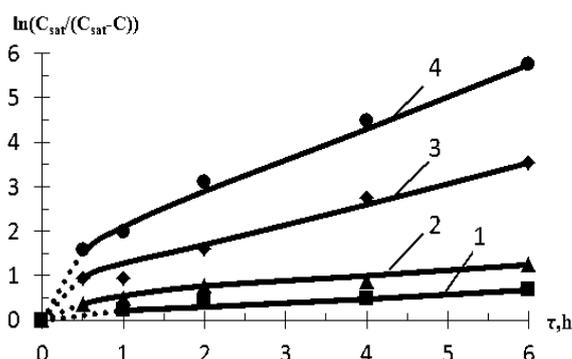
The results suggest that TG transition from the ballistic material into the aquatic environment is determined by the TG dissolution. In this case we can assume the following model. Let at this transition during the time  $d\tau$ , TG concentration in the aquatic environment as a consequence of its dissolution will change for  $dC$ . It can be assumed that for this time period the transition speed is proportional to  $C_{sat} - C$ . Then the equation can be written  $dc/d\tau=K(C_{sat}-C)$ , (1) where  $k$  - the proportionality coefficient (of mass transfer),  $s^{-1}$ .

After the equation (1) integration taking into account the fact that when  $\tau=0$ , the TG concentration in water  $C=0$ , we will obtain:  $K\tau=\ln(C_{sat}/C_{sat}-C)$  (2)

The formula for calculating the current value of TG concentration in water can be obtained from the equation (2)  $C=C_{sat}(1-e^{-K\tau})$  (3)

In accordance with the fact that the equation (2) is linear, in this case, the coefficient  $K$  was determined directly from the equation using the experimental data.

Such representation of the experimental data, which is shown in the Fig. 3 shows that the linear relation corresponding to the equation (2), is observed in the prolonged contact with water. On TG transition in the initial stage the diffusion processes are obvious overlapped and the mechanism doesn't correspond to the accepted model. Also when conducting the experimental research at this stage there is uncertainty with the assessment of the contact duration associated with the sample ballistic material loading, its wetting and uploading.



**Figure 3.** The experimental data representation according to the equation (2) for various process conditions: 1 -  $t=35$  °C,  $G_0=1,0 \cdot 10^{-3}$  kg,  $V=0,4 \cdot 10^{-3}$  m<sup>3</sup>; 2 -  $t=20$  °C,  $G_0=1,0 \cdot 10^{-3}$  kg,  $V=0,1 \cdot 10^{-3}$  m<sup>3</sup>; 3 -  $t=35$  °C,  $G_0=1,0 \cdot 10^{-3}$  kg,  $V=0,1 \cdot 10^{-3}$  m<sup>3</sup>; 4 -  $t=35$  °C,  $G_0=2,0 \cdot 10^{-3}$  kg,  $V=0,1 \cdot 10^{-3}$  m<sup>3</sup>.

The data for the coefficient  $K$  determination in the conditions of ballistic material prolonged contact with water is shown in the Fig. 4. They show that the coefficient  $K$  increases with the increasing of the process temperature Fig. 4a, TG amount of introduced into the system from the original ballistic material Fig. 4b and it decreases with the water environment volume increasing.

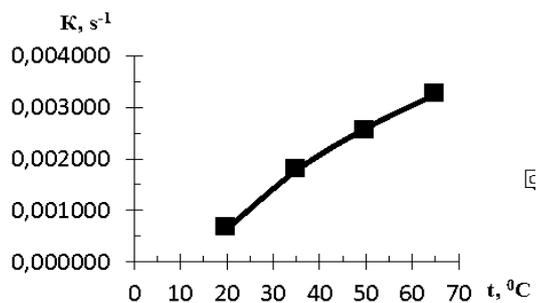


Fig. 4a

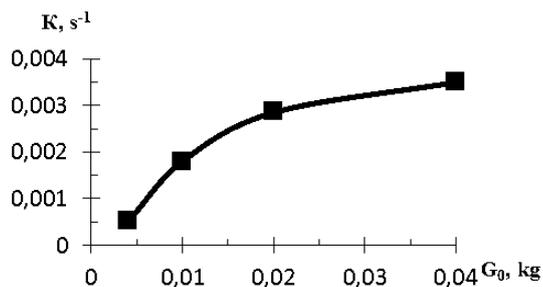


Fig. 4b

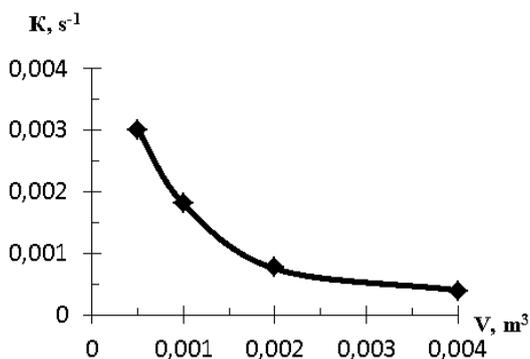


Fig. 4c

**Figure 4.** The dependences of the coefficient K from the process parameters: a - the temperature, b - the amount of TG loading, c - the water environment volume.

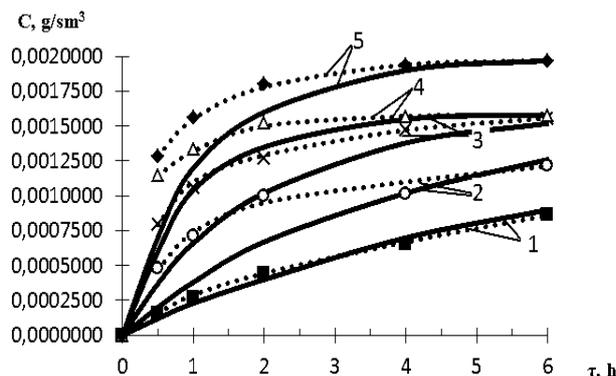
Mathematical processing of this data allowed obtaining an empirical equation relating the coefficient K with the specified process parameters

$$K = 0,176 \cdot 10^{-6} \cdot t^{1,28} \cdot C_{pot}^{0,93}, s^{-1} \quad (4)$$

where  $C_{pot}$  - combined parameter ( $kg/m^3$ ), according to the physical meaning corresponding to the TG maximum (potential) concentration in water (concentration, which can be achieved in full TG transition from the ballistic material at the absence of water saturation) is equal to the  $C_{pot} = G_0/V$ .

Obtained dependencies (3) and (4) allow calculating the TG concentration change in water under specified conditions of its transition from the ballistic material.

The comparison of such calculation results with the experimental data Fig. 5 shows that the long-term contact of the ballistic material with the aquatic environment, the TG transition into the water is well described by the model of TG dissolution in the water.



**Figure 5.** The comparison of TG concentrations in the aquatic environment (solid lines) calculations results with the experimental data (dotted line) at the different process conditions: 1 -  $t=35^{\circ}C$ ,  $G_0=1,0 \cdot 10^{-3} kg$ ,  $V=0,4 \cdot 10^{-3} m^3$ ; 2 -  $t=35^{\circ}C$ ,  $G_0=1,0 \cdot 10^{-3} kg$ ,  $V=0,2 \cdot 10^{-3} m^3$ ; 3 -  $t=35^{\circ}C$ ,  $G_0=1,0 \cdot 10^{-3} kg$ ,  $V=0,1 \cdot 10^{-3} m^3$ ; 4 -  $t=35^{\circ}C$ ,  $G_0=1,0 \cdot 10^{-3} kg$ ,  $V=0,05 \cdot 10^{-3} m^3$ ; 5 -  $t=50^{\circ}C$ ,  $G_0=1,0 \cdot 10^{-3} kg$ ,  $V=0,1 \cdot 10^{-3} m^3$ .

### Conclusions

1. Mixing the ballistic material particles in the aquatic environment TG, which is the part of this material, is partially transferred to the aqueous environment.

2. Transition speed and resulting solution concentration increase with the increase of TG amount, which is entered from the original ballistic material, the process temperature and the decrease the aquatic environment volume. At the same time TG concentration approaches to the saturated solution concentration.

3. The TG transition process from the ballistic material in the aquatic environment in general is not limited by its diffusion in the ballistic material, while at the initial stage it may affect in transition.

4. On the basis of suggested TG transition into the water model, the calculated dependences are obtained to determine the resulting solution concentration with long-term contact of the ballistic material with water.

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