



## Some Kinetic Regularities of the Polycondensation of Glycols with Carboxy-containing Compounds in the Synthesis of Polyester Resins for Tin Containers Coating



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CURRENTLY, the biggest share of paints and varnishes intended for painting internal surface of metal canning containers is accounted for by compositions containing epoxy oligomers. Despite the fact that such materials allow to obtain coatings with good adhesion to metal substrates, sufficient chemical resistance and elasticity, they have one significant drawback, which is due to the main component of epoxy resins – bisphenol A.

Due to the well-known negative effects of bisphenol A on human health, the use of such materials is currently limited.

Promising replacement of these materials are composites based on polyester resins.

However, it should be mentioned that the disadvantage of polyester varnishes intended for canning containers is the low resistance of coatings to sterilization when laying food products in containers. The main reason for such low resistance is a relatively high content of ester groups in the structure of these polymers, characterized by low water, alkali and limited acid resistance.

To increase the resistance of such coatings, we proposed to introduce fragments of unsaturated monomers (capable of homopolymerization under the conditions of polyester compositions (intended for can-coating) curing) into the composition of their polymer macromolecules.

These fragments should create an additional steric hindrance for diffusion to ester groups of destructive molecules of aggressive media and ensure the durability of coatings in general.

Synthesis of such polyesters is a typical polycondensation process, and to accelerate it, it is advisable to use various catalytic systems.

**Keywords:** Polyester resins, Can coatings, Varnishing of tin, Kinetics of polycondensation.

### Introduction

One of the types of packaging containers for canned food are cans made of white tin, chrome steel or aluminum in sheet or tape form. This container is necessarily provided with the coating (varnished), with the result that eliminates metal corrosion or any effect of the metal on the quality of the product [3]. Can coatings are produced subject to very high requirements for elasticity, resistance to solvents and chemicals, as well as to the content of toxic components [1].

Usually, varnishes produced on the basis of high-molecular epoxy and/or phenolic resins are used as protective internal varnishes [2]. All epoxy resins used contain fragments of 4, 4' diphenylolpropane (bisphenol A), including simple 2,2'-bis-(4-hydroxyphenyl)propane-bis(2,3-epoxypropyl)ester, as well as its homologues, also known as bisphenol-A-diglycidyl esters.

Since the beginning of the XXI century, the world has seen the biggest activity in the study of the effects of bisphenol A and its derivatives on the

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human body. In recent decades, it has been clearly proved that this substance and its derivatives have a negative impact on the human endocrine system. It is known that bisphenol-A-diglycidyl esters, when tested “in vitro”, shows mutagenic and carcinogenic effects, even with the migration of ultra-small amounts of these substances from the lacquer film into packaged food [6].

When polyesters used as the main binder, there are wide opportunities in the field of designing materials with the necessary properties [3]. Some authors [4, 5] describe materials based on pure polyesters; thereat, high-quality physical and mechanical properties are noted. However, the scope of use of such compositions is limited to the color of the metal profile (the so-called “coil-coating”), which does not involve manufacture of containers for food products. Also, the disadvantage of such materials [5] is a significant amount of solvent (more than 70%), which worsens the environmental friendliness of the material and increases the consumption rate when using it, in them. In addition, the use of “heavy” solvents, on which the authors’ works are based, predetermines their migration into the embedded product, which negatively affects its quality.

The most promising direction in the creation of environmentally friendly coatings, in our opinion, is the development of materials based on polyester resins.

A variety of amino-containing products are used as cross-linking agents (cross-linkers) of polyester resins. Curing polyesters with such cross-linkers is formally close to curing compositions based on epoxy resins for canning containers. Coatings based on such compositions must have sufficient adhesion, flexibility, resistance to stretching and bending.

So the authors of the invention [7] suggest the use of polyesters and polyesteracrylates to eliminate bisphenol-A-diglycidyl esters for the production of coatings with good adhesive properties. The patent [8] proposed a method for producing a water-soluble polyester composition, which also does not contain bisphenol-A-diglycidyl esters, with high physical and mechanical properties, along with satisfactory resistance to sterilization in water. However, the formulas of both compositions include methanolized hexamethylenemelamine that suggests a potential migration of such harmful substances like methanol and formalde-

hyde from the varnish film, while the data on migration of these substances in the document are missing. However, such a way has limitations because of the toxicity of most of these cross linkers.

Therefore, our proposed approach to the directed change of the structure of the polyester molecule design, in order to obtain a one-component composition, is essentially unique.

The chosen direction is extremely relevant both for practical purposes, consisting in the possibility of technologically convenient way to synthesize polyesters for canned varnishes, and for fundamental science in terms of development of ideas concerning the class of polyester resins [9, 10].

The process of condensation of neopentyl glycol trimers with phthalic and maleic anhydride with a possible co-monomer – terephthalic acid - was considered as the object of research.

## **Methods**

The synthesis was carried out in a reaction vessel equipped with a typical binding. Control of synthesis was carried out by acid number. After the synthesis was completed, the obtained polyesters were analyzed by the medium viscosity molecular weight, glass transition temperature, acid and hydroxyl number.

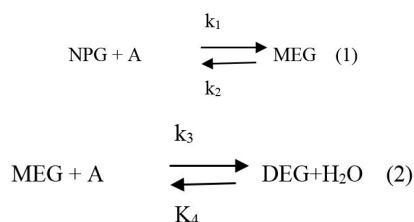
To construct a kinetic model of the condensation process of neopentylglycol with anhydrides in the presence of monobutyltin oxide, a reaction tank equipped with a standard binding was used. In the study of kinetic regularities of the process of esterification of neopentylglycol with phthalic anhydride, the excess of glycol (4.9 mol) relative to the anhydride (1.0 mol) was taken as the base ratio, and in the study of kinetic regularities of the process of esterification of neopentylglycol with maleic anhydride; the excess of glycol (3.75 mol) relative to the anhydride (1.0 mol) was taken as the base ratio; as with such a ratio, the process ends with the receipt of trimers, with a small amount of dimeric molecules. Since glycol in both cases was taken in a significant excess, the amount of catalyst was tied to the content of carboxylic components and was 0.1% of the mass of their number. The temperature regime for research was in the range of 150-200°C. Control over the change in the content of functional groups was carried out by titrimetric method, by changing the concentration of the functional group of the initial monomers. The mixing intensity in the limit of up

to 1.5 m/s to ensure the flow of the process in the kinetic region, i.e. a chemical reaction will be the limiting stage of the process.

Control over the change in the concentration of the initial substances was carried out at specified intervals for each of the syntheses, by sampling and analysis, by titrimetric method of the content of carboxylic (determination of acidic chill, AN) and hydroxyl (determination of hydroxyl number, HN) components.

#### Test report

On the basis of the putative mechanism of the interaction of glycols with carboxyl-containing components, the process of condensation of neopentylglycol (NPG) with anhydrides (A) with the formation of dimers (monoesterglycol MEG) and trimers (diester glycol DEG) can be represented in a system of consecutive reversible reactions:



where  $k_1$ - $k_6$  is the reaction rate constant,  $l/(\text{mol} \cdot \text{min})$ .

Based on the assumptions made for the condensation of neopentylglycol with anhydrides, the following kinetic equations were obtained:

- anhydride consumption rate,  $l/(\text{mol} \cdot \text{min})$ :

$$w_a = d[A]/dt = -k_1[\text{NPG}][A] + k_2[\text{MEG}]$$

- the rate of formation of dimers (monoesters of neopentylglycol),  $l/(\text{mol} \cdot \text{min})$ :

$$w_{\text{MEG}} = d[\text{MEG}]/dt = k_1[\text{NPG}][A] - k_2[\text{MEG}] - k_3[\text{MEG}][A] + k_4[\text{DEG}][\text{H}_2\text{O}]$$

- the rate of formation of trimers (diesters of neopentylglycol),  $l/(\text{mol} \cdot \text{min})$ :

$$w_{\text{DEG}} = d[\text{DEG}]/dt = k_3[\text{MEG}][A] - k_4[\text{DEG}][\text{H}_2\text{O}]$$

The Runge-Kutta method implemented in the software product MATLAB R2009a was used for mathematical processing of experimental data and evaluation of kinetic constants included in the generalized model of the process. Minimization of the relative sum of the squared deviations of the calculated values of the concentrations of the reaction mixture components from the experimental ones throughout the array of experimental

data was chosen as a criterion for calculation of constants. The results of calculation of the rate constants at different temperatures are shown in Table 1.

The Arrhenius equation was used to describe the temperature dependences of the reaction rate constants.

Figures 1 and 2 show a graphical representation of the temperature dependence of the rate constants of the interaction of neopentylglycol with phthalic and maleic anhydrides, respectively, expressed by the Arrhenius equation.

The results of calculation of the Arrhenius equation parameters are shown in Table 2. Parameters and their confidence intervals are determined at a significance level of 0.05 (95% confidence probability).

The adequacy of the obtained kinetic model of the processes of condensation of neopentylglycol with anhydrides in the presence of monobutyltin oxide was evaluated using the Fisher criterion at a significance level of 0.05 (95% confidence probability). The value of the repeatability variance ( $S^2_{\text{repeatab.}}$ ) was 0.0832; dispersion of adequacy ( $S^2_{\text{adeq.}}$ ) - 0.0059. Experimental value of the Fisher criterion ( $F_{\text{exp.}}$ ) was 0.08 at the critical value of the Fisher criterion ( $F_{\text{cr.}}$ ) equal to 1.67. Since the experimental value of the Fisher criterion is less than the critical one, the obtained kinetic equations adequately describe the experimental data.

On the basis of the obtained mathematical model, optimization of the modes of condensation of neopentylglycol with anhydrides was carried out. The optimization results are shown in Table 3.

Due to the fact that the composition of the studied system includes terephthalic acid, which has an extremely high melting point, it was decided (in order to establish the completeness of the picture) first to investigate the kinetics of reactions occurring in the model medium.

For such a model environment, we have chosen a system consisting of the following components: di-neopentyl-glycol-maleinate, p-toluic acid, monobutyltin oxide. The choice of neopentylglycol maleinate as a modeling compound was determined by the data on the condensation of neopentylglycol with various anhydrides, see Tables 1 and 2. These data show that despite the fact that maleic anhydride

TABLE 1. Calculated values of the rate constants

Temperature, K	Reaction rate constant, l/(mol min)			
	$k_1$	$k_2$	$k_3$	$k_4$
Condensation of neopentylglycol with phthalic anhydride				
423	$0.72 \cdot 10^{-3}$	$0.031 \cdot 10^{-3}$	$0.63 \cdot 10^{-3}$	$0.45 \cdot 10^{-3}$
433	$0.98 \cdot 10^{-3}$	$0.052 \cdot 10^{-3}$	$1.02 \cdot 10^{-3}$	$0.78 \cdot 10^{-3}$
443	$1.34 \cdot 10^{-3}$	$0.134 \cdot 10^{-3}$	$1.54 \cdot 10^{-3}$	$1.23 \cdot 10^{-3}$
453	$1.78 \cdot 10^{-3}$	$0.254 \cdot 10^{-3}$	$2.18 \cdot 10^{-3}$	$1.76 \cdot 10^{-3}$
463	$2.01 \cdot 10^{-3}$	$0.379 \cdot 10^{-3}$	$2.34 \cdot 10^{-3}$	$1.95 \cdot 10^{-3}$
Condensation of neopentylglycol with phthalic anhydride				
423	$1.03 \cdot 10^{-3}$	$0.065 \cdot 10^{-3}$	$0.95 \cdot 10^{-3}$	$0.67 \cdot 10^{-3}$
433	$1.27 \cdot 10^{-3}$	$0.084 \cdot 10^{-3}$	$1.32 \cdot 10^{-3}$	$1.04 \cdot 10^{-3}$
443	$1.49 \cdot 10^{-3}$	$0.187 \cdot 10^{-3}$	$1.67 \cdot 10^{-3}$	$1.36 \cdot 10^{-3}$
453	$2.08 \cdot 10^{-3}$	$0.371 \cdot 10^{-3}$	$2.38 \cdot 10^{-3}$	$1.99 \cdot 10^{-3}$
463	$2.27 \cdot 10^{-3}$	$0.604 \cdot 10^{-3}$	$2.51 \cdot 10^{-3}$	$2.18 \cdot 10^{-3}$

TABLE 2. Calculated values of activation energy  $E_A$  and preexponential factor  $k_{0i}$ 

Parameter	Neopentylglycol- phthalic anhydride	Neopentylglycol- maleic anhydride
	value	value
$E_{a1}$ , kJ/mol	$72.06 \pm 0.5$	$81.4 \pm 0.5$
$E_{a2}$ , kJ/mol	$24.7 \pm 0.3$	$27.9 \pm 0.5$
$E_{a3}$ , kJ/mol	$51.6 \pm 0.5$	$67.3 \pm 0.5$
$E_{a4}$ , kJ/mol	$39.4 \pm 0.5$	$54.8 \pm 0.5$
$k_{01}$ , l/(mol·min)	$(1.07 \pm 0.04) \cdot 10^{10}$	$(1.21 \pm 0.05) \cdot 10^{10}$
$k_{02}$ , l/(mol·min)	$(3.45 \pm 0.05) \cdot 10^2$	$(3.79 \pm 0.05) \cdot 10^2$
$k_{03}$ , l/(mol·min)	$(2.17 \pm 0.04) \cdot 10^6$	$(3.59 \pm 0.05) \cdot 10^6$
$k_{04}$ , l/(mol·min)	$(5.76 \pm 0.04) \cdot 10^3$	$(4.92 \pm 0.05) \cdot 10^3$

is more reactive than phthalic anhydride, the absolute difference in the kinetic parameters is not great, in addition, maleic anhydride contains an unsaturated double bond, which can affect the polarization of the system, changing it.

Study of kinetics of reactions occurring in the specified system was carried out at a temperature of 180-220°C. The concentration of p-toluic acid varied from 0.1 to 0.6 mol/l. Monobutyltin oxide in an amount of 0.02-0.10 mol/L.

The composition of the reaction products was determined by the methods of gas-liquid chromatography and IR spectroscopy, functional and elemental analysis.

It was found that the composition of the products, *ceteris paribus* is largely determined by

the reaction temperature.

Thus, at a temperature of 180-190°C, a monosubstituted product of the interaction of p-toluic acid with dineopentylglycolmaleinate is formed in the reaction system, which was isolated and identified by counter synthesis. The analysis data is shown in Table 4 and Fig. 3.

We found that the rate of homocondensation of p-toluic acid (PTA) with an acid catalysis at a temperature of 190-220°C in the presence of monobutyltin oxide (Cat) is described by the following equation:

$$w_r = k_r [PTA]^2 \cdot [Cat] \quad (3)$$

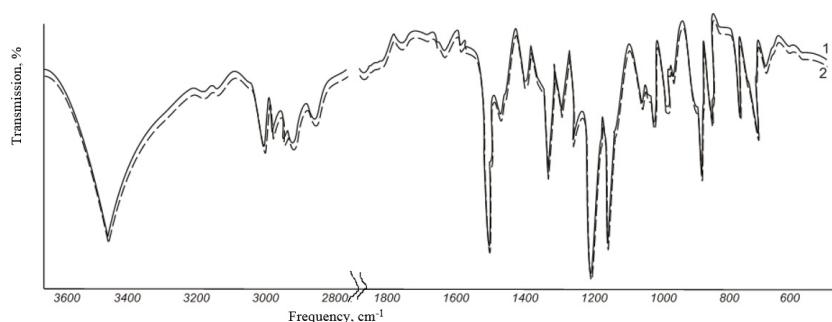
With a further increase in temperature (above 200°C) in the reaction system, a change in the

**TABLE 3.** The technological parameters of the process of condensation of neopentylglycol with phthalic and maleic anhydrides in the presence of monobutyltin oxide

Serial No.	Technological parameter	Value
Neopentylglycol - phthalic anhydride		
1	Temperature, °C	180
2	The molar ratio of neopentylglycol - anhydride	4.9 – 1.0
3	Concentration of monobutyltin oxide catalyst, % wt	0.1
4	Duration of the condensation process, min	420
5	Degree of completion of reaction	0.94
6	The output of the trimer, %	84.2
neopentylglycol – maleic anhydride		
7	Temperature, °C	160
8	The molar ratio of neopentylglycol - anhydride	3.75 – 1.00
9	Concentration of monobutyltin oxide catalyst, % wt	0.1
10	Duration of the condensation process, min	440
11	Degree of completion of reaction	0.96
12	The output of the trimer, %	81.7

**TABLE 4.** Analysis data of the selected product and mono p-toluic ester of dineopentylglycolmaleinate obtained by counter synthesis

Reaction product	Melting point, °C	Elemental composition, % weight. C - H	OH-groups content, %	Molecular weight	Relative retention time for gas-liquid chromatography method at T=250°C
Isolated	174.4	67.8 – 15.9	4.40	380+5	24
Mono p-toluic ester of dineopentylglycolmaleinate	175	64.7 – 17.6	4.38	388	24

**Fig. 1.** IR spectra of the isolated product (1) and 2 mono p-toluic ester of dineopentylglycolmaleinate obtained by the counter synthesis of (2)

process pattern is observed. Thus, by the method of gas-liquid chromatography and elemental analysis, the isolated products of reactions occurring in this system at temperature of 210°C were identified.

They are mono-p-toluic ester dineopentylglycolmaleinate (MPTKE) and di-p-toluic ester for dineopentylglycolmaleinate (DPTCE). Kinetic curves of changes in concentrations of the agent and reaction products: shown in Fig. 4.

A series of experiments in which the concentration of 2 ptolui acid was changed in the range from 0.1 to 1.0 mol/L. Thus, it is noted that the share of products of esterification in the system decreases with increasing initial concentration of ptoluic acid (Table 5).

Thus, at a temperature of 210°C and an initial concentration of ptoluic acid not exceeding 0.5 mol/l, two reactions occur in the reaction system according to the scheme:

Moreover, these reactions are studied in conditions of flow as practically not in equilibrium. The reaction rate constants of both reactions are calculated and given in Table 6.

On the basis of the experimental data obtained, it can be concluded that the following system of differential equations is suitable for calculating the kinetic parameters for the processes in the system under consideration, occurring in the temperature range of 180-220°C:

$$-d[\text{PTA}]/dt = k_m[\text{PTA}] \cdot [\text{Cat}] + k_d[\text{PTA}]^2 \cdot [\text{Cat}] \quad (4)$$

$$d[\text{DPTCE}]/dt = k_g[\text{PTA}]^2 \cdot [\text{Cat}] \quad (5)$$

$$d[\text{MPTCE}]/dt = k_e[\text{PTA}] \cdot [\text{Cat}] \quad (6)$$

The adequacy of the obtained kinetic model of the process of reaction of ptoluic acid with trimers of neopentylglycol and maleic in the presence of monobutyltin oxide was evaluated using the Fisher criterion at a significance level of 0.05 (95% confidence probability). The value of the repeatability variance ( $S^2_{\text{repeatab.}}$ ) was 0.0794; dispersion of adequacy ( $S^2_{\text{adeq.}}$ ) - 0.0078. Experimental value of the Fisher criterion ( $F_{\text{exp.}}$ ) was 0.09 at the critical value of the Fisher criterion ( $F_{\text{cr.}}$ ) equal to 1.34. Since the experimental value of the Fisher criterion is less than the critical one, the obtained kinetic equations adequately describe the experimental data.

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Comparison of the calculated and experimental values of the concentration in the reaction mixture is shown in Fig. 3. Deviation of the calculated values from the experimental ones does not exceed 10 %.

Thus, a satisfactory coincidence of experimental and calculated curves of changes in the concentration of the initial reagents and reaction products proves the validity of the proposed reaction schemes.

The obtained data can be used as a basis for technological regimes of the process of condensation of terephthalic acid with trimers of neopentylglycol and anhydrides. Table 7 presents the recommended modes of this process.

Thus, on the basis of experimental studies to establish the effect of the temperature regime on the kinetic features of interaction of the systems under consideration, practical recommendations were given for the synthesis of safe innovative nanostructured polyester resins for protection of can containers.

### Discussion of the results

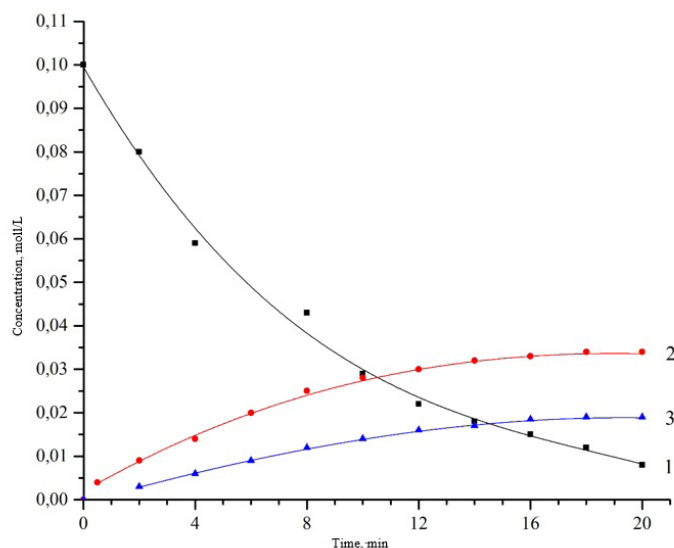
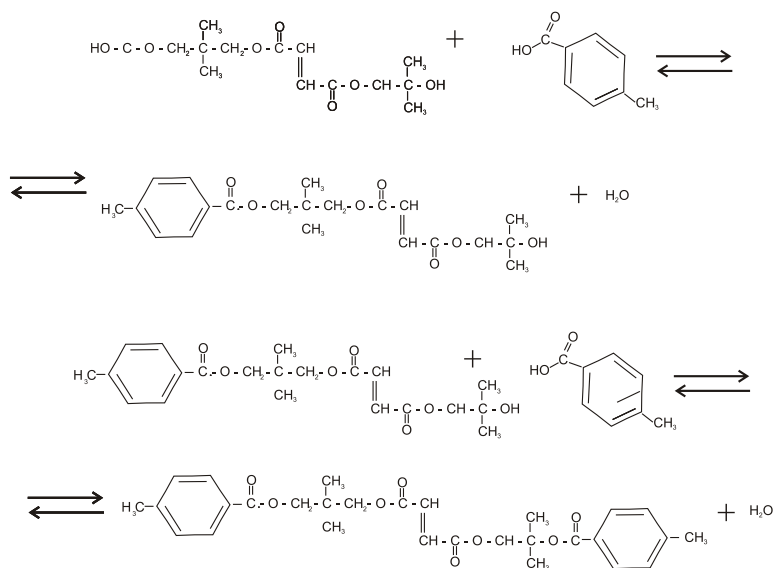
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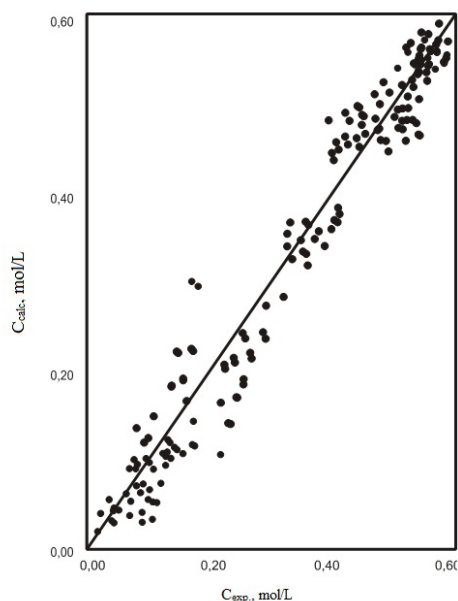
The possibility of directed control of technological parameters, including those

**TABLE 5. Dependence of the ratio of the reaction products (in mole %) in the system of p-toluic acid - monobutyltin oxide, at a temperature of 210°C, reaction time is 24 hours, the concentration of monobutyltin oxide is 0.08 mol/L.**

The initial concentration of p-toluic acid, mol/l	0.1	0.3	0.5	0.7	1.0
Content of mono p-toluic ester of dineopentylglycolmaleinate, %	63.0	46.7	51.0	80.0	75.0
Content of di-p-toluic ester of dineopentylglycolmaleinate, %	19.0	5.66	4.82	-	-
Ratio of mono - and di - substitution products	0.3	0.12	0.09	-	-



**Fig. 2. Kinetic curves of change in concentration of p-toluic acid (1), mono-p-toluic ester of dineopentylglycolmaleinate (2) and di-p-toluic ester of dineopentylglycolmaleinate (3) in the reaction system of p-toluic acid - monobutyltin oxide at a temperature of 210°C. The initial concentration of p-toluic acid - 0.1 mol/L. Concentration of monobutyltin oxide - 0.08 mol/L.**



**Fig. 3.** Comparison of experimental and calculated concentrations in the reaction mixture of ptoluic acid with trimers of neopentylglycol and maleic one in the presence of monobutyltin oxide.

**TABLE 6.** Rate constants of the reactions of mono (km) and di-substitution (kd) in the system of ptoluic acid - monobutyltin oxide. Concentration of monobutyltin oxide – 0.08 mol/L, temperature 210°C.

Concentration of ptoluic acid, mol/L	0.1	0.3	0.5	0.7	1.0
km, L <sup>2</sup> /(mol <sup>2</sup> ·s)	10 <sup>-1</sup> ·8.58	10 <sup>-1</sup> ·5.9	10 <sup>-2</sup> ·8.97	10 <sup>-3</sup> ·10.0	10 <sup>-3</sup> ·0.95
kd, L <sup>2</sup> /(mol <sup>2</sup> ·s)	1.0310 <sup>-4</sup>	10 <sup>-4</sup> ·0.93	10 <sup>-4</sup> ·0.87	-	-

**TABLE 7.** The technological parameters of the process of condensation of terephthalic acid with trimers neopentylglycol with phthalic and maleic anhydrides in the presence of monobutyltin oxide

Serial No.	Technological parameter	Value
neopentylglycol - phthalic anhydride		
1	Temperature, °C	200 - 220
2	Molar ratio of terephthalic acid – trimer of neopentylglycol with phthalic anhydride – trimer of neopentylglycol with maleic anhydride	2.0 – 1.333 – 0.667
3	Concentration of monobutyltin oxide catalyst, % wt	0.1
4	Duration of the condensation process, min	4400
5	The degree of completion of the reaction by acid, %	91.3



presented in Table 7, allows us to control the change in the structure of polyester, formed during the synthesis, which ultimately determines the performance properties of coatings based on it, such as elasticity, resistance to scratching, physical and chemical ones, including wetting, fluidity, adhesion, as well as the target ones - the ability to cure under certain conditions and resistance to sterilization in model environments

### **Conclusion**

The work results allow not only to answer some theoretical issues associated with the pattern of synthesis of the polyesters, but also to consider features of zooming of the technology in the transfer of laboratory data to experimental and industrial plants. It should be noted that tin can varnishes and enamels are used for production of a wide range of metal containers, which, in turn, are subject to fundamentally different requirements. For example, for a solid-drawn can, first of all, a good elongation is important, which makes it necessary to obtain a coating with good elasticity and adhesion. In the manufacture of a composite can, resistance to press-work is important, that causes the varnish film resistance to impact and bending. For internal coatings of containers, it is necessary to resist model environments, and for external ones - primarily, attention is paid to the decorative properties and resistance to scratching, etc.

Attention is drawn to the fact that tin containers are made both of black metal with different treatment, namely:

- white hot-dipped tin-plate for cans (HDTP);
- white electrolytic tin-plate for cans (ETP, ETP-D);
- black tin for cans (BTC);

and of non-ferrous metals, namely:

- food grade anodized aluminum;
- food grade aluminum with chromate phosphate coating;

etc.

Naturally, all these substrates would have different wetting and flow behaviour, which, of course, should be taken into account when developing polyester systems. The research carried out in this work will allow to introduce a new safe product into the market of tin varnishes

and enamels. Use of this product will improve the efficiency of food preservation technology, by improving the safety (elimination of toxic and carcinogenic substances) during preservation and storage.

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