



Features of Polyester Resins in Terms of Their Use for Varnishing Canning Containers, with Improved Stamping Resistance



Nikolay A. Apanovich*, Elena Yu. Maksimova, Alexandra D. Zelenskaya, Anton V. Alekseenko, Alexander V. Pavlov, Denis D. Kapitonov

D. Mendeleev University of Chemical Technology of Russia, Moscow, Russian Federation

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 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. The main reason for such low resistance is a relatively high proportion of ester groups, 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 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.

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 [1]. 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 [2].

Usually, varnishes produced on the basis of high-molecular epoxy and/or phenolic resins are used as protective internal varnishes [3]. All epoxy resins used contain fragments of 4,4' diphenylpropane (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 human body. In recent decades, it has been clearly

*Corresponding author e-mail: apanovichnikolay@rambler.ru

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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 [4].

When polyesters used as the main binder, there are wide opportunities in the field of designing materials with the necessary properties [2]. Some authors [5, 6] 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 formaldehyde 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 [9-12].

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.

Based on the literature data for the poly - and esterification reaction, substances that increase the activity of the carboxylic component are most effective as a catalytic system, and the catalysis process proceeds based on the cation mechanism. Use of substances that increase the activity of the hydroxyl-containing component is undesirable, because of the probability of initiating side reactions.

Because the synthesized product is intended for use in can coating, then, except for selective activity, the catalysts are required to meet a number of requirements of the environmental plan, it is desirable that these substances were safe for humans during their migration into the food. Thus, the use of compounds of heavy metals, organic and a number of mineral acids as catalysts is unacceptable. Therefore, industrial catalysts used for the esterification process were chosen. It should be noted that in case of catalysts that include tin and contain organic anions, it was necessary to have dietary allowance (FDA).

Calcium oxide, calcium carbonate, potassium carbonate, sodium bicarbonate, calcium octoate (availability of FDA), monobutyltin oxide (availability of FDA) and orthophosphoric acid were selected as basic catalytic systems.

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 evaluate the properties of the synthesized polyesters, varnish was prepared by dissolving them in a mixture of organic solvents, cross-linker and surface additives were added to obtain a working viscosity of 120-130 seconds according to the viscometer VZ-4, with a mass fraction of non-volatile substances $50\pm 3\%$ by weight. Then the coating was applied to the substrate (white tin ETP II class) with a dry film thickness of 6-8 g/m². Curing was carried out in a convection oven at a temperature of 195-200°C for 15 minutes.

First, the assessment of the following decorative and physico-mechanical properties of coatings was carried out:

- coating appearance;
- elongation with a coefficient of 0.6 (GOST 29309);
- film adhesion before sterilization (GOST 15140 method 2);
- coating impact strength (GOST 4765);
- film tensile strength (GOST 29309).

In case of successful completion of the tests, according to these indicators, the resistance of coatings to sterilization in drinking water at a temperature of 120°C for one hour was evaluated, as well as adhesion after sterilization (GOST 5981, GOST 5717 and GOST 25749) [13]. Sterilization was carried out on cups with a coefficient of elongation of 0.6, manufactured under GOST 29309.

To compare the catalytic activity of the selected catalysts, trial syntheses were carried out at a temperature of 200°C, with the addition of a catalyst in an amount of 0.5% of the total mass. The analysis was carried out at regular intervals for each of the syntheses, by sampling and calculating the degree of completion of the reaction by acid, with titrimetric method (acid number determination).

Test report

Intact substances were selected with the following ratio: trimer of neopentylglycol with phthalic anhydride – 1.333 mol, trimer of neopentylglycol with maleic anhydride – 0.667 mol; also, xylene in the amount of 3.0% of the total weight was introduced for azeotropic distillation.

the results are shown in Table 1 and Fig. 1.

When monobutyltin oxide is used as a catalyst, after 300 minutes the output of acid of about 90 % is reached. Orthophosphoric acid showed comparable catalytic activity, but after the process, during storage of polyester synthesized with its use, there was a spontaneous increase in viscosity, which is an undesirable factor.

Potassium carbonate and sodium bicarbonate in general showed good results, but during storage of polyesters synthesized with their use, there was a formation of white precipitate. Analysis of this precipitate, using IR and NMR, showed that its basis is unreacted terephthalic acid (limit degree of completion for these polyesters is 0.80-0.83).

Therefore, further studies were carried out with monobutyltin oxide.

Since monobutyltin oxide is a commercial product, with a degree of purity of “ч” class (i.e. it contains the main component of 98.0% and above), it consists of various impurities, including moisture, which reduce its catalytic activity. Figure 2 shows the IR spectrum of commercial monobutyltin oxide (a), monobutyltin oxide calcined at 250°C (b) and calcined monobutyltin oxide, after exposure for 3 days in the air (relative humidity 67%) (b).

As can be seen from the above spectrum, after calcination of monobutyltin oxide, bands with intensity of 3600 -3650 cm⁻¹, which correspond to the associated OH-groups (due to air moisture sorption), disappear from the spectrum; however, the intensity of the bands in the region of 1400 cm⁻¹ corresponding to O-C-O bonds increases, which may be due to sorption of carbon dioxide from the air when calcined on the catalyst surface. Exposure of calcined monobutyltin oxide in air leads to re-adsorption of moisture (spectra (a) and (b) practically coincide).

Thus, it becomes obvious that the commercial product contains a significant amount of sorption-bound water, which should adversely affect its catalytic activity. To check this assumption, studies have been conducted to establish the influence of heat treatment of monobutyltin oxide on its activity.

Commercial monobutyltin oxide was calcined at temperatures of 120-200°C for 2 h directly prior to catalytic testing. To eliminate the effect of carbon dioxide sorption, calcination was carried

TABLE 1. Catalytic activity of different acid type catalysts in the process of condensation of trimers of neopentylglycol with phthalic and maleic anhydride with a co-monomer – terephthalic acid

Time, min.	The degree of completion of the reaction by acid, weight content						
	CaO	CaCO ₃	K ₂ CO ₃	NaHCO ₃		C ₄ H ₁₀ O ₂ Sn	H ₃ PO ₄
0	0.00	0.00	0.00	0.00	0.00	0.00	0.00
60	0.15	0.17	0.20	0.21	0.13	0.25	0.24
120	0.26	0.29	0.37	0.38	0.20	0.44	0.42
200	0.39	0.44	0.54	0.56	0.32	0.65	0.62
260	0.50	0.57	0.69	0.72	0.45	0.84	0.80
300	0.53	0.60	0.74	0.76	0.50	0.89	0.85
360	0.57	0.63	0.78	0.81	0.55	0.94	0.90
400	0.58	0.65	0.80	0.83	0.57	0.96	0.92

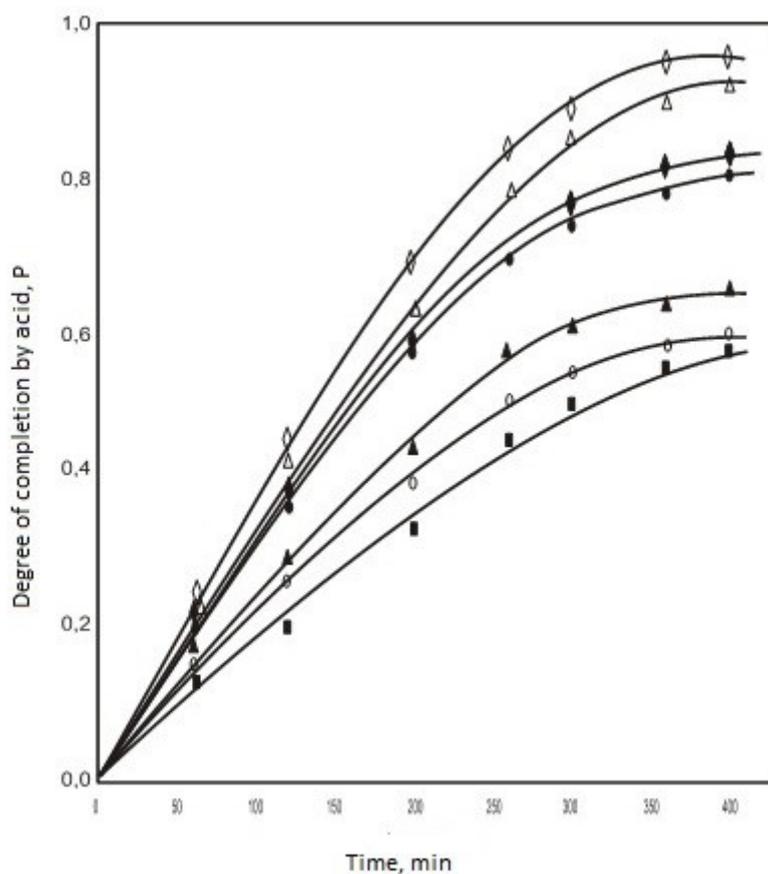


Fig. 1. The catalytic activity of various catalysts in condensation of trimers of neopentylglycol with phthalic and maleic anhydride with a co-monomer – terephthalic acid, the amount of catalyst is 0.5 % by weight., temperature – 200°C; ○ – CaO; ▲ – CaCO₃; ● – K₂CO₃; ◆ – NaHCO₃; ■ – Ca(C₈H₁₅O₂)₂; ◇ – C₄H₁₀O₂Sn; Δ – H₃PO₄

out in an inert gas (nitrogen) current.

The effect of the calcination temperature on the catalytic activity in the condensation of trimers of neopentylglycol with phthalic and maleic anhydride with a co-monomer – terephthalic acid is shown in Fig. 3. The results of the study are given in Table 2.

As a result of studies, it was found that the biggest catalytic activity was shown by a sample calcined at a temperature of 150°C, in the air current. At this temperature, there is almost complete evaporation of water, (see Fig. 4).

At the same time, such a technological method as calcination can have its disadvantages, which consist in partial sintering of the initial catalyst powder. After calcination with the powder, partial sintering occurs, which, due to an increase in the apparent specific surface area of the catalyst, reduces its efficiency. Therefore, to remove sorbed water from the surface of monobutyltin oxide, it is advisable to offer an alternative method of heat treatment.

We proposed to introduce into the catalytic system based on monobutyltin oxide the compounds, which, on the one hand, effectively bound the water molecules on its surface, and contribute to the increase in its efficiency on the other hand, i.e. would serve as co-catalysts.

We proposed to use orthophosphoric acid derivatives as being such compounds. Two factors caused this decision. First, orthophosphoric acid has a fairly high hygroscopicity, and second, it has shown itself well as a catalyst for the process under consideration. Of course, as shown above, it has one significant drawback – it catalyzes the process of three-dimensional polycondensation of the resulting polyester during storage. However, in our opinion, its derivatives, due to the lower reactivity, should be deprived of such a disadvantage.

The following elements were selected as the derivatives of orthophosphoric acid: compound ester of aminospirit choline, glycerine, phosphoric and linoleic acid (soybean phospholipid), diglycidyl ester of phosphoric acid and 2ethylhexan-1-ol phosphoric acid.

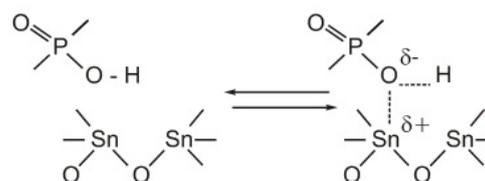
These three components are commercially available products, they are used as catalysts, polarizing additives and are, respectively, di- and monosubstituted phosphoric acid.

When using the above compounds, the increase in catalytic activity is due to the formation of coordination bonds between the negative charge on the co-catalyst and Sn^{IV} ions. In order to study the influence of co-catalysts on the catalytic activity of monobutyltin oxide, the catalyst samples were dispersed (immediately prior to the synthesis process of the polyester) in the liquid phase of the catalyst taken in the amount of 10 mol %, at an angular velocity of 20.0 m/s, for 30 minutes.

After dispersion, the samples were analyzed using IR spectroscopy. When treating monobutyltin oxide with soybean phospholipid (see Fig. 5), the bands corresponding to fluctuations of OH connection in OH-groups disappear from the spectrum, while a shift of the band of phospholipid at 3430 with 3470cm⁻¹ is observed.

A similar pattern is observed when reading the spectra of monobutyltin oxide treated with diglycidyl ester of phosphoric acid and 2ethylhexane-1-ol of phosphoric acid. An interesting fact is the shifts on the spectra in the region of 900 – 1600 cm⁻¹, for all three studied systems, (Fig. 5-7), which cause oscillations of groups of type -O-C_nH_{2n+1}, -O-C- and -P-O-

The obtained data of IR spectroscopy suggest that the interaction of monobutyltin oxide with derivatives of phosphoric acid on its surface formed OH - and -P-O- groups, according to the proposed scheme:



Thus, pretreatment of monobutyltin oxide with derivatives of phosphoric acid increases the polarizability of the active centers of the catalyst, and thus should enhance its activity in the process of condensation of trimers of neopentylglycol with phthalic and maleic anhydride with a co-monomer – terephthalic acid. The results of a study of the effect of pretreatment of monobutyltin oxide on the rate of this process are shown in Table 3.

From the data of Table 3 it can be seen that during condensation of trimers of neopentylglycol with phthalic and maleic anhydride with a co-monomer – terephthalic acid pretreated

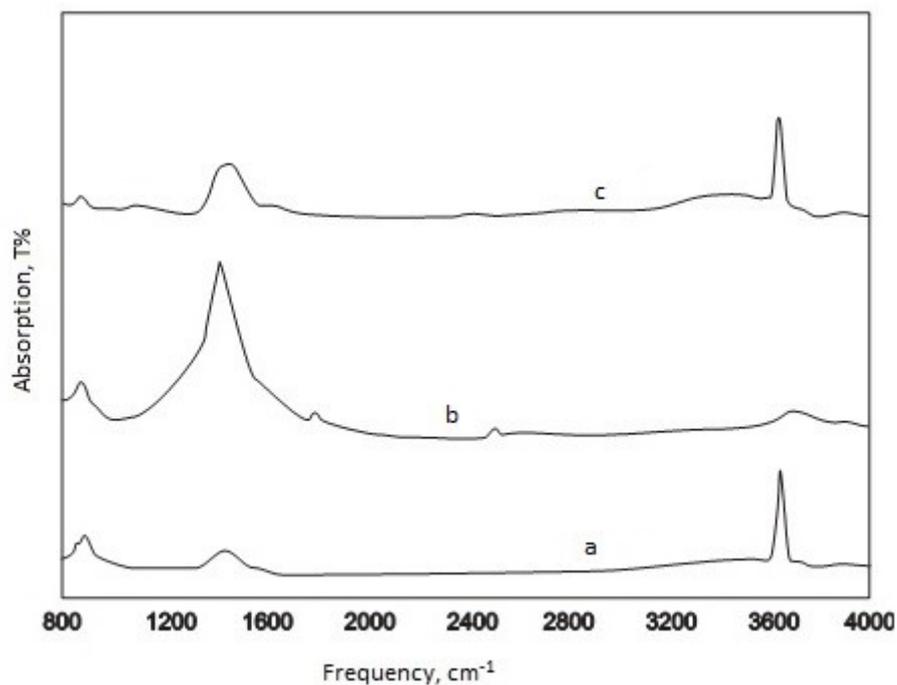


Fig. 2. The IR spectrum of commercial monobutyltin oxide (a), calcined at a temperature of 250°C (b) and calcined monobutyltin oxide after exposure for 3 hours in air.

TABLE 2. Effect of temperature of calcination on the catalytic activity of monobutyltin oxide in the process of condensation of the trimers of neopentylglycol with phthalic and maleic anhydride with a co-monomer – terephthalic acid at a temperature of synthesis – 200°C

Time, min.	The degree of completion of the reaction by acid, weight content at the calcination temperature, °C			
	without calcination	120	150	200
0	0.00	0.00	0.00	0.00
60	0.25	0.26	0.31	0.45
120	0.44	0.46	0.65	0.79
200	0.65	0.70	0.84	0.91
260	0.84	0.88	0.91	0.93
300	0.89	0.92	0.93	0.95
360	0.94	0.96	0.97	0.98
400	0.96	0.97	0.98	0.99
460	0.96	0.97	0.98	0.99
520	0.96	0.97	0.98	0.99

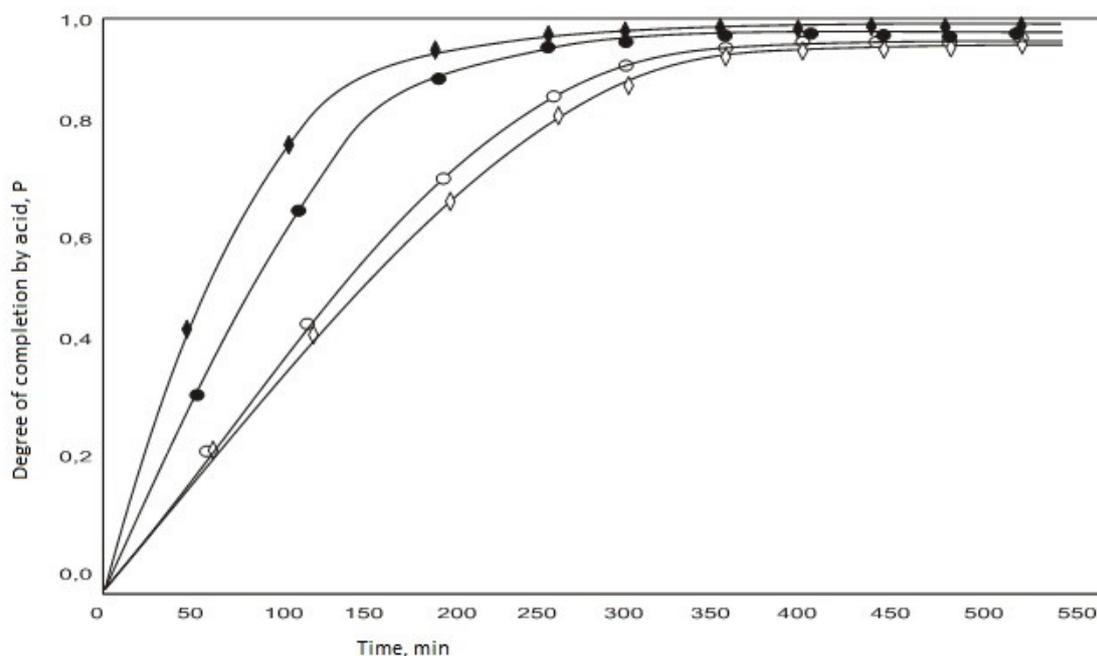


Fig. 3. The effect of the temperature of calcination of monobutyltin oxide on the reaction rate of condensation of trimers of neopentylglycol with phthalic and maleic anhydride with a co-monomer – terephthalic acid, at a synthesis temperature of 200°C; ◇ – monobutyltin oxide (commercial); ○ – monobutyltin oxide, calcined at 120°C; ● – monobutyltin oxide, calcined at 150°C; ◆ – monobutyltin oxide, calcined at 200°C

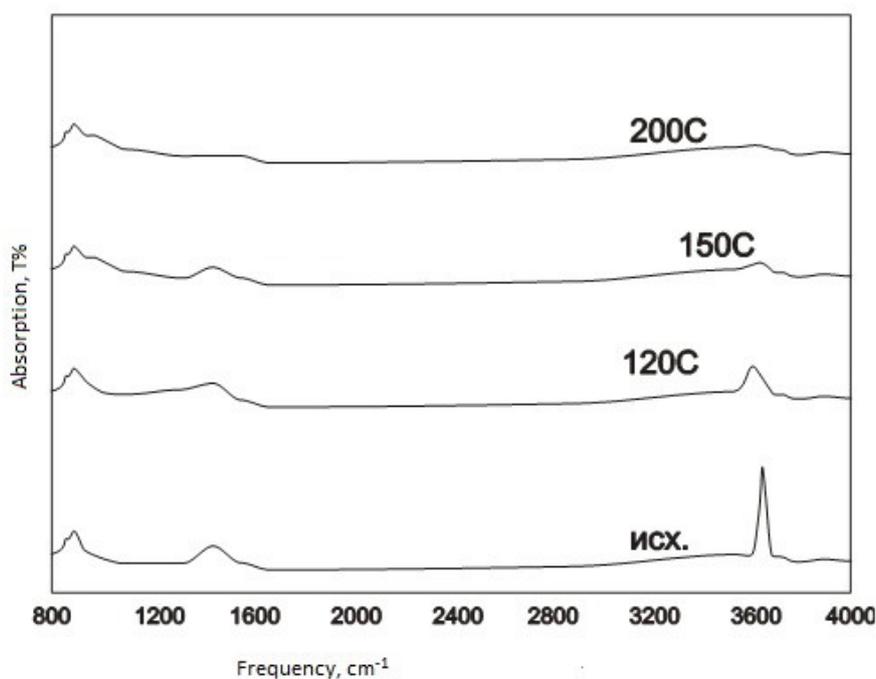


Fig. 4. The IR spectrum of monobutyltin oxide samples, calcined under different conditions.

catalyst, the process rate increases sharply, both in comparison with the untreated catalyst - monobutyltin oxide, and in comparison with the calcined monobutyltin oxide.

The greatest effect is achieved when aminospirit choline, glycerine, linoleic acid and phosphoric acid (soybean phospholipid) are used as a co-catalyst of a compound ester.

Thus, our studies showed that for effective implementation of the process of condensation of trimers of neopentylglycol with phthalic and maleic anhydride with a co-monomer - terephthalic acid, it is advisable to use monobutyltin oxide in combination with co-catalyst - compound ester of aminospirit choline, glycerine, linoleic acid and phosphoric acid (soybean phospholipid). Use of a co-catalyst leads to formation of a polarization complex characterized by high catalytic activity.

Discussion of the results

In the course of this work we have investigated the effect of different catalytic systems on condensation of trimers of neopentylglycol with phthalic and maleic anhydride with a co-monomer - terephthalic acid.

Use of the basic laws of polycondensation processes in combination with modification allows obtaining coatings with the required performance properties on the basis of one-component polyester materials.

Despite the fact that modification of polymer molecules is a fairly common technique to change their properties. Works on the directed regulation of the composition of polyesters used in the production of can containers, which differs with quite specific requirements, have not been carried out to date.

Despite the fact that in fact, the chemistry of the synthesis of polyesters is reduced to the interaction of a hydroxyl-containing component with a carboxyl-containing one, and, theoretically, these laws are described in the literature, the real processes are influenced not only by the ratio of the carboxyl equivalent to the hydroxyl one, the type and concentration of the catalyst, but also by the relative activity of functional groups and the order of their introduction, even with linear polycondensation.

The possibility of a directed change in the structure and deepening the degree of completion

of the reaction due to the introduction of catalytic systems and, as a consequence, data on the effect of a monomer fragment in a polyester macromolecule will allow to predict in advance how the qualitative and quantitative composition of the initial monomer mixture would affect such physical and mechanical properties as glass transition temperature, elasticity, scratch resistance, physical and chemical, including wetting, fluidity, adhesion, as well as the target ones - the ability to cure under certain conditions and resistance to sterilization in model media

Conclusion

The work results allow not only to answer some theoretical aspects 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.

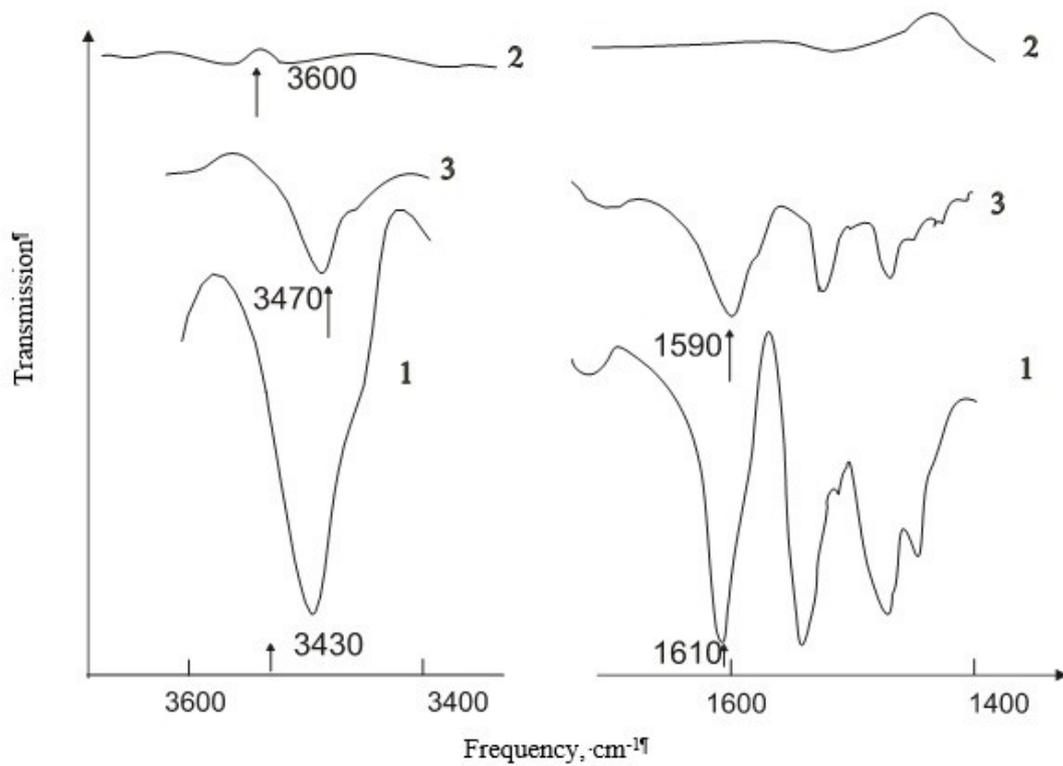


Fig. 5. Fragments of the IR spectrum of the soybean phospholipid (1), monobutyltin oxide (2) and monobutyltin oxide treated with phospholipid (3)

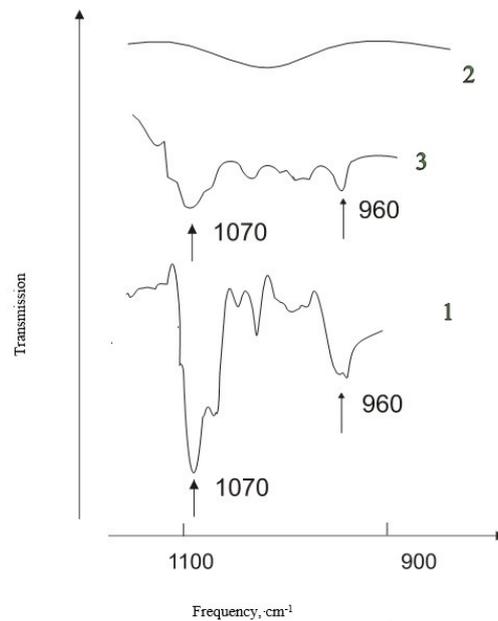


Fig. 6. Fragments of the IR spectra of diglycidylester ester of phosphoric acid (1), monobutyltin oxide (2) and monobutyltin oxide treated with diglycidyl ester of phosphoric acid (3)

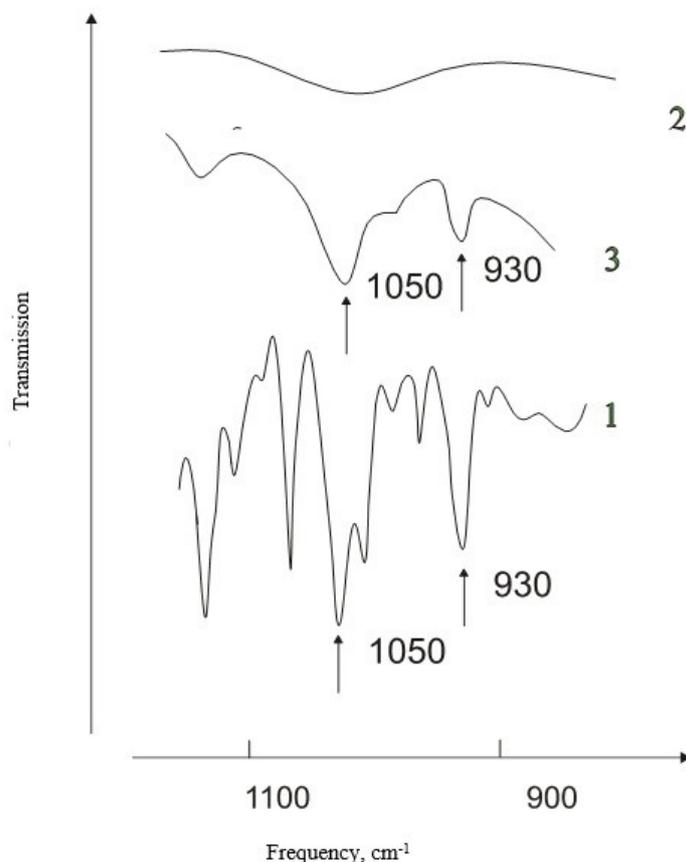


Fig. 7. Fragments of the IR spectrum 2ethylhexan-1-ol phosphoric acid (1), monobutyltin oxide (2) and monobutyltin oxide treated with 2ethylhexan-1-ol phosphoric acid (3)

TABLE 3. Effect of treatment on the catalytic activity of monobutyltin oxide in the process of condensation of the trimers of neopentylglycol with phthalic and maleic anhydride with a co-monomer – terephthalic acid at a temperature of synthesis – 200°C

Time, min.	The degree of completion of the reaction by acid, weight content at the calcination temperature, °C				
		heat treatment at 150°C	soybean phospholipid treatment	treatment with diglycidyl ester of phosphoric acid	treatment and 2ethylhexan-1-ol phosphoric acid
0	0.00	0.00	0.00	0.00	0.00
60	0.25	0.26	0.45	0.38	0.32
120	0.44	0.46	0.68	0.52	0.50
200	0.65	0.70	0.84	0.78	0.73
260	0.84	0.88	0.95	0.92	0.93
300	0.89	0.92	0.97	0.96	0.96
360	0.94	0.96	0.98	0.96	0.97
400	0.96	0.97	0.99	0.97	0.98
460	0.96	0.97	0.99	0.98	0.99
520	0.96	0.97	0.99	0.98	0.99

Naturally, all these substrates would have different wetting and flow behavior, which, of course, should be taken into account when developing polyester systems.

The research carried out in this work will allow introducing 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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