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Investigation of the Effect of Reactive Diluent on the Properties of Coatings Based on Unsaturated Polyesters

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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, Reactive diluent.

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 supplied with a coating (varnished). The main purpose of these coatings is to prevent contact between the metal and the container filler (food), thereby eliminating corrosion of the metal or any metal effects on the product quality [1]. Needless to say, the varnish layer should in no way affect or cause damage to the filler, for example, due to dissolving or migrating components of the varnish. That is why, coating agents and 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 for packages of sheet metal [3]. 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. It is known that bisphenol-A-diglycidyl esters, when tested “in vitro”, shows mutagenic and carcinogenic effects, even with the migration

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of ultra-small amounts of these substances from the lacquer film into packaged food [4].

SpecialChem company conducted a survey among specialists in the field of development of paints and varnishes on possible ways of replacement in materials based on epoxy resins. As a result of the survey, 36.2% of researchers named the modification of epoxy resins by replacing bisphenol A with other bisphenols, for example, F and C, or with various diglycidyl esters, such as: resorcinol diglycyl ester, 1,4-cyclohexandimethanol diglycyl ester, neopentylglycol diglycyl ester, 2-methyl-1,3-propanol diglycyl ester and bis-epoxide obtained from 2,2,4,4-tetramethyl-1,3-cyclobutanediol. This allows you to keep the proven technology of the use of conventional epoxy compositions. The disadvantages of this direction include information on the toxicity of bisphenols F and C and the limited availability of the mentioned diglycidyl esters [5, 6].

28.7% of researchers supported the development of can varnishes and paints based on polyester resins. When polyesters used as the main binder, there are wide opportunities in the field of designing materials with the necessary properties [2]. Some authors [7, 8] 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 [8] 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.

At the same time, 20.5% of researchers supported the development of varnishes and paints based on polyurethanes. Polyurethane materials allow obtaining coatings with good decorative properties. When using polyurethane materials there are two main problems – their high cost and toxicity of diisocyanates. One way to minimize these problems is to combine the chemical properties of polyurethanes with the chemical properties of polyesters. Combination of the advantages of these two classes of compounds will minimize the amount of diisocyanate used in the resin.

Non - bisphenol-A-diglycidyl esters of the coating for roll coating of sheet metal are described in a number of patents offering usage of polyesters in combination with blocked polyisocyanates in materials for varnishing cans [9]. The authors note high physical and mechanical properties of coatings based on such materials. However, blocked polyisocyanates (during hot drying) cleave suitable locking agent, for example, butanonoxime or e-caprolactam. However, these cleaved substances do not meet GN 2.3.3.97 2-00 "Maximum permissible amount of substances emitted from materials contacting with foodstuff" (2000), and may partially remain in the varnish layer, and then migrate into the filler. Therefore, usage of such varnish systems in the internal varnishing of canned food containers is questionable.

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 production of coatings with good adhesive properties. The patent [7] 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.

Thus, in the materials used for varnishing tin cans, there is a tendency to replace epoxy and epoxy-phenolic materials that do not contain bisphenol A polyester compositions. In all materials devoted to the development of polyester materials, the authors follow the path of varying the composition of materials – a combination of different types of cross-linkers with polyester matrices.

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 presence of unsaturated fragments in the structure of a polyester molecule allows the use of reactive diluents – low molecular weight compounds that act as crosslinking agents, but chemically embedded in the polymer network during formation of coatings.

Reactive solvent - styrole - is the most widespread agent for this type of polyesters in the industry [10, 11]. Since copolymerization of styrole is strongly inhibited by air oxygen, a pop-up additive (paraffin) is introduced into the varnish, due to which oxygen access to the generated film is excluded. Paraffin is introduced as a 3% solution in styrole in an amount of 0.1—0.3% from the weight of the varnish. After applying the varnish to the surface, the paraffin floats, forming a surface layer that prevents contact with air oxygen. After complete curing of the coating, the paraffin-containing layer is removed by grinding. Curing of such varnishes in the presence of accelerators (e.g. manganese octoate or cobalt naphthenate) occurs at room temperature. However, the viability of styrole-containing polyester compositions after the introduction of the initiating system is very small (up to 30 min), and special methods are required for their application [10]. Therefore, use of styrole as an active diluent of polyesters when varnishing tin intended for the manufacture of tin containers, due to the low viability is impossible. Often, compositions based on unsaturated polyesters as active diluents include acrylates. Dimethacrylic ester triethylene glycol, produced as TGM-3, showed the best efficiency. However, formation of coatings based on such compositions requires not only accelerators, but also polymerization initiators – peroxides, for example, cumene hydroperoxide, cyclohexanone peroxide or isopropylbenzene hydroperoxide [11].

One of the most interesting types of active diluents are derivatives of allyl alcohol, this is due to the fact that allyl groups are able to self-activate in interaction with air oxygen, i.e. the products of the primary interaction of this group with oxygen are the initiators of further cross-linking of polymer macromolecules [10, 11]. Diallyl ester of trimethylolpropane and allylglycidyl ester are the most widespread in the industry. It should be noted that the application of these active diluents also requires data on the migration of harmful substances during storage of foodstuff in cans.

Therefore, our 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 [7, 9, 12, 13].

Methods

The curing processes of compositions with polyesters containing unsaturated fragments are based on the reactions of radical copolymerization by double bonds of polyesters and monomers (active solvents) [14]. A significant role in this process is played by reactions involving air oxygen, the so-called oxidative polymerization. To assess the physical, mechanical and operational properties of coatings based on polyester compositions with reactive diluents, varnishes were prepared by dissolving polyesters in a mixture of organic solvents, with the addition of reactive diluents in an amount of 1.0 to 40.0% of weight, to obtain a system with a working viscosity of 120-140 seconds by viscometer VZ-4, with a mass fraction of non-volatile substances 50$\pm$3% weight; cross-linkers based on benzoguanamine derivatives were also introduced. After preparation of varnishes, coatings were applied to the substrate (white tin ETP (electrolytic tin-plate for cans), class II) with a rod applicator until the dry film thickness reaches 6-8 g/m^2. Curing was carried out in a convection oven at a temperature of 195 $^{\circ}$C for 15 minutes. First, assessment of the following decorative and physico-mechanical properties of coatings was carried out:

- coating appearance;
- elongation with a coefficient of 0.6;
- film adhesion before sterilization;
- coating impact strength;
- film tensile strength.

Table 1 presents data on the assessment of decorative and physical-mechanical properties of coatings with reactive diluents of various types.

From these data it can be seen that the best indicators for adhesive strength (8,0 – 12,0 MPa) are observed in systems containing glycidyl methacrylate and allylglycidyl ester as reactive diluents, as we expected, there is the effect of the glycide group on the adhesion interaction with the metal. However, the resistance of coatings to drawing on the basis of compositions with these diluents with a content of glycidyl methacrylate of more than 10.0% and a content of allylglycidyl ester of more than 20.0% is unsatisfactory; after drawing, cracks and rips are formed on the coating. This behavior is most likely due to the fact that an increase in the active diluent leads to an increase in the density of the polymer network, and it becomes more rigid, while the coating loses its elasticity. The fact that for systems containing methylcidyl methacrylate and alliglycidyl ester as reactive diluents, film tensile strength decreases with the growth of their content, proves our assumption.

When using triethylene glycol dimethacrylic ester as an active diluent, the results were generally satisfactory in the range of concentrations under consideration. However, it should be noted that the value of adhesive strength for coatings based on it is relatively high and is about 4.5 -5.5 MPa. This fact can be explained by the structure of this reactive diluent – there are no fragments in its composition that would contribute to the improvement of adhesive strength. Systems with trimethylolpropane diallyl ester showed the worst results. When the content of this diluent exceeds 1.0% by weight, multiple defects in the form of craters and resist points appear on the coating, with a content of more than 30.0% by weight, there is a “fish eye” defect. Only when the content of the trimethylolpropane diallyl ester equaled to 1.0% by weight, the coatings had a satisfactory appearance, resisted to drawing with a coefficient of 0.6, but the adhesive strength was only 4.0 MPa, while the tensile strength of the film was 5.0 mm. In our opinion, this behavior in the case of the trimethylolpropane diallyl ester is associated with its chemical structure, this substance contains two allyl fragments capable of copolymerization with unsaturated fragments of polyester synthesized by us, which apparently leads to an extremely high cross-linking density, which worsens the extract. Presence of a free hydroxyl group, in our opinion, accelerates the crosslinking process also by the condensation mechanism, which significantly accelerates the formation of coatings, while the “hardening” of the coating quickly occurs, and the solvent molecules “tear” the formed film when evaporating, leading to the formation of the above defects. Coating defects, of course, reduce the physical and mechanical properties, primarily affecting the adhesive strength. Therefore, before further tests start, to assess the resistance of coatings to sterilization, systems containing glycidyl methacrylate with a content of up to 10.0% by weight, inclusive, were allowed as reactive diluents for sterilization; alliglycidyl ester with a content of up to 20.0% by weight, inclusive, and triethylene glycol dimethacrylic ester with a content of 1.0 to 40.0 by weight. Evaluation of resistance to sterilization in drinking water was carried out in a laboratory autoclave at a temperature of 120ºC for one hour, on cups with a coefficient of elongation of 0.6, manufactured under GOST 29309-92; adhesion after sterilization was evaluated as well. The results of the coating tests, five cups batches, based on the studied compositions, are presented in table 2.

As can be seen from the data presented in table 2, sterilization resistance was demonstrated by the coatings with composition based on synthesized polyester with reactive solvents:

- glycidylmethacrylate, 5.0% by weight.;

- glycidylmethacrylate, 10.0% by weight.;

- allylglycidyl ester, 5.0% by weight;

- allylglycidyl ester, 10.0% by weight.

It should be noted that the maximum adhesive strength after sterilization (from 10.5 to 11.5 MPa) was observed in the composition containing 10% of glycidylmethacrylate by weight, which is slightly more than in the case of a composition that does not contain a reactive diluent (from 9.5 to 10.5 MPa). Coatings based on the above composition were evaluated for environmental safety by analyzing the migration of harmful substances from these coatings in accordance with GN 2.3.3.972-00.

As a result of the analysis, it turned out (see table 3) that on the coatings based on a composition consisting of synthesized polyester with a reactive diluent – glycidyl methacrylate (10% by weight), migration from glycidylmethacrylate coating in the amount of 0.004 mg/L (drinking water) and

TABLE 1. Evaluation of the properties of coatings based on synthesized polyesters with the addition of reactive diluents

Reactive diluent content, % by weight	Coating appearance;	Drawing resistance with a coefficient of 0.6	Film adhesion before sterilization, point;	Film adhesion before sterilization, normal tear, MPa	Coating impact strength, cm;	Film tensile strength, mm.
1	2	3	4	5	6	7
Without reactive diluent						
-	Transparent	Resist.	1	12.0	50	8.5
Dimethacrylic ester of triethylene glycol (TGM-3)						
1.0	Transparent	Resist.	1	4.5	50	7.5
3.0	Transparent	Resist.	1	5.0	50	7.5
5.0	Transparent	Resist.	1	5.5	50	7.5
10.0	Transparent	Resist.	1	5.5	50	7.5
20.0	Transparent	Resist.	1	5.0	50	7.5
30.0	Transparent	Resist.	1	4.5	50	7.5
40.0	Transparent	Resist.	1	4.5	50	7.5
Glycidylmethacrylate						
1.0	Transparent	Resist.	1	4.5	50	6.5
3.0	Transparent	Resist.	1	4.5	50	7.5
5.0	Transparent	Resist.	1	8.0	50	8.5
10.0	Transparent	Resist.	1	12.0	50	8.5
20.0	Transparent	Cracks	1	2.0	50	5.5
30.0	Transparent	Cracks	1	2.0	50	5.5
40.0	Transparent	Cracks	1	2.0	50	5.0
Trimethylolpropane diallyl ester						
1.0	Transparent	Resist.	1	4.0	50	5.0
3.0	Transparent, craters	Cracks	1	3.0	50	4.5
5.0	Transparent, craters	Cracks	2	2.0	50	4.5
10.0	Transparent, Craters, resist spots	Cracks	2	2.5	50	4.5
20.0	Transparent, craters, resist spots	Rips	2	2.0	50	4.5
30.0	Transparent, craters, resist points, “fish eye”	Rips	3	Less than 2.0	50	3.0
40.0	Transparent, craters, resist points, “fish eye”	Rips	3	Less than 2.0	50	3.0
Allylglycidyl ester						
1.0	Transparent	Resist.	1	4.5	50	7.0
3.0	Transparent	Resist.	1	5.5	50	7.5
5.0	Transparent	Resist.	1	10.5	50	8.5
10.0	Transparent	Resist.	1	12.0	50	8.5
20.0	Transparent	Resist.	1	8.0	50	5.5
30.0	Transparent	Cracks	2	2.0	50	4.5
40.0	Transparent	Cracks	2	2.5	50	4.5

TABLE 2. Evaluation of resistance to sterilization of coatings based on synthesized polyesters with different types of reactive diluents

Sample No.	Reactive diluent content, % by weight	Resistance to sterilization (visual)	Film adhesion after sterilization, point;	Film adhesion after sterilization, normal tear, MPa
1	**2**	**3**	**4**	**5**
		Without reactive diluent		
1	-	Resistant	1	9.5-10.5
		Triethylene glycol dimethacrylate ester		
1	1.0	Multiple rips	3	Less than 2.0
2	1.0	Multiple rips	3	Less than 2.0
3	1.0	Multiple rips	2	2.0
4	1.0	Multiple rips	2	2.0
5	1.0	Multiple rips	3	Less than 2.0
		Triethylene glycol dimethacrylate ester		
1	3.0	Multiple rips	3	Less than 2.0
2	3.0	Multiple rips	2	2.0
3	3.0	Multiple rips	2	2.0
4	3.0	Multiple rips	2	2.0
5	3.0	Multiple rips	3	Less than 2.0
		Triethylene glycol dimethacrylate ester		
1	5.0	Small rips	2	2.5
2	5.0	Small rips	2	2.0
3	5.0	Small rips	2	2.0
4	5.0	Small rips	2	2.0
5	5.0	Small rips	3	Less than 2.0
		Triethylene glycol dimethacrylate ester		
1	10.0	Small rips	2	2.5
2	10.0	Small rips	2	2.5
3	10.0	Small rips	2	2.0
4	10.0	Small rips	2	2.0
5	10.0	Small rips	2	2.5
		Triethylene glycol dimethacrylate ester		
1	20.0	Multiple rips	2	2.5
2	20.0	Multiple rips	3	2.0
3	20.0	Multiple rips	3	Less than 2.0
4	20.0	Multiple rips	2	2.0
5	20.0	Multiple rips	3	Less than 2.0

TABLE 2. Continuation

1	2	3	4	5
		Triethylene glycol dimethacrylate ester		
1	30.0	Multiple rips	2	Less than 2.0
2	30.0	Multiple rips	3	Less than 2.0
3	30.0	Multiple rips	3	Less than 2.0
4	30.0	Multiple rips	2	2.0
5	30.0	Multiple rips	3	Less than 2.0
		Triethylene glycol dimethacrylate ester		
1	40.0	Multiple rips	3	Less than 2.0
2	40.0	Multiple rips	2	2.5
3	40.0	Multiple rips	3	Less than 2.0
4	40.0	Multiple rips	2	2.0
5	40.0	Multiple rips	2	2.0
		Glycidylmethacrylate		
1	1.0	Small rips	3	2.0
2	1.0	Small rips	2	2.0
3	1.0	Small rips	3	Less than 2.0
4	1.0	Small rips	2	2.0
5	1.0	Small rips	2	2.0
		Glycidylmethacrylate		
1	3.0	Small rips	3	Less than 2.0
2	3.0	Small rips	2	2.0
3	3.0	Small rips	3	Less than 2.0
4	3.0	Small rips	3	Less than 2.0
5	3.0	Small rips	2	2.0
		Glycidylmethacrylate		
1	5.0	Resistant	1	6.0
2	5.0	Resistant	1	5.5
3	5.0	Resistant	1	5.5
4	5.0	Resistant	1	5.0
5	5.0	Resistant	1	5.5
		Glycidylmethacrylate		
1	10.0	Resistant	1	11.0
2	10.0	Resistant	1	10.5
3	10.0	Resistant	1	10.5
4	10.0	Resistant	1	11.0
5	10.0	Resistant	1	11.5

TABLE 2. Continuation

1	2	3	4	5
		Allylglycidyl ester		
1	1.0	Small rips	2	2.5
2	1.0	Small rips	3	2.0
3	1.0	Small rips	2	2.5
4	1.0	Small rips	2	2.0
5	1.0	Small rips	2	2.5
		Allylglycidyl ester		
1	3.0	Small rips	2	2.5
2	3.0	Small rips	2	2.5
3	3.0	Small rips	2	2.5
4	3.0	Small rips	2	3.0
5	3.0	Small rips	2	2.5
		Allylglycidyl ester		
1	5.0	Resistant	1	6.5
2	5.0	Resistant	1	7.0
3	5.0	Resistant	1	7.5
4	5.0	Resistant	1	6.5
5	5.0	Resistant	1	6.5
		Allylglycidyl ester		
1	10.0	Resistant	1	8.5
2	10.0	Resistant	1	9.0
3	10.0	Resistant	1	8.5
4	10.0	Resistant	1	9.0
5	10.0	Resistant	1	9.0
		Allylglycidyl ester		
1	20.0	Small rips	2	3.5
2	20.0	Small rips	2	2.5
3	20.0	Small rips	2	2.0
4	20.0	Small rips	2	3.0
5	20.0	Small rips	3	2.0

TABLE 3. Evaluation of ecological security of the coatings based on the composition consisting of the synthesized polyester with a reactive diluent – glycidylmethacrylate in the amount of 10% by weight, according to GN 2.3.3.972-00

Controlled value	Model environment	DCM, mg/l	Test result	ND on research methods
Phenol	Drinking water	0.100	Absent	MU 4395-87
	Distilled water		Absent	
Formaldehyde	Drinking water	0.100	Absent	MU 4395-87
	Distilled water		Absent	
Epichlorohydrin	Drinking water	0.100	Absent	MU 4395-87
	Distilled water		Absent	
Diphenylolpropane	Drinking water	0.100	Absent	MU 4395-87
	Distilled water		Absent	
Lead (Pb)	Drinking water	0.03	Absent	GOST 18293
	Distilled water		0.0002	
Zinc (Zn)	Drinking water	1.00	Absent	GOST 18293
	Distilled water		Absent	
Methyl alcohol	Drinking water	0.200	Absent	МУ 94272-
	Distilled water		Absent	
Propyl alcohol	Drinking water	0.100	Absent	МУ 94272-
	Distilled water		Absent	
Butyl alcohol	Drinking water	0.500	Absent	МУ 94272-
	Distilled water		Absent	
Isobutyl alcohol	Drinking water	0.500	Absent	МУ 94272-
	Distilled water		Absent	
Acetone	Drinking water	0.100	Absent	МУ 94272-
	Distilled water		Absent	
Derivatives of acrylic acids (methacrylates)	Drinking water	0.25	0.004	МУ 94272-
	Distilled water	0.25	0.006	

0.006 mg/L (distilled water) is observed, which is significantly lower than the permissible migration concentration of 0.25 mg/L.

On the basis of this composition, a batch of covers of SKO “182” type, in the amount of 60 pieces, and a batch of covers of “twist-off” type, in the amount of 60 pieces, were made for evaluation of stamping feature. For a sample batch of these stamped caps (10 pieces), evaluation of sterilization resistance in distilled water at a temperature of 120ºC for one hour was carried out, in accordance with GOST 25749, the test results are presented in table 4.

As it can be seen, with a decrease in temperature from 195 to 170ºC, the adhesive strength deteriorates sharply. So, once the coating is formed at 170ºC, it is a total of 3.0 MPa, compared to 12.0 MPa at 195^{0}C. At the same time, lowering the temperature improves the strength of the film under tension, at a temperature of 170175^0-C, it is 8.0 mm, while it is 7.5 mm at a temperature of 195^{0}C. From the analysis of the data on sterilization of coatings formed at different temperatures, at a temperature of 120ºC for one hour, on cups with a coefficient of elongation of 0.6, manufactured in accordance with GOST

TABLE 4. Evaluation of resistance to sterilization of covers of SKO “1-82” type and “twist-off” type on the basis of the composition consisting of the synthesized polyester with a reactive diluent – glycidylmethacrylate in the amount of 10% by weight.

Sample no.	Resistance to sterilization (visual)	Film adhesion after sterilization, point;	Film adhesion after sterilization, normal tear, MPa
	“Twist-off” SKO type covers		
1	Resistant	1	11.5
2	Resistant	1	11.0
3	Resistant	1	10.0
4	Resistant	1	10.5
5	Resistant	1	11.5
6	Resistant	1	10.5
7	Resistant	1	10.0
8	Resistant	1	10.5
9	Resistant	1	11.0
10	Resistant	1	10.5
	Covers of SKO type “1-82”		
1	Resistant	1	10.5
2	Small rips on the outer diameter	1	10.0
3	Resistant	1	11.0
4	Resistant	1	11.5
5	Resistant	1	11.5
6	Resistant	1	10.5
7	Resistant	1	10.0
8	Small rips on the outer diameter	1	9.5
9	Resistant	1	11.5
10	Resistant	1	11.0

TABLE 5. Evaluation of the properties of coatings based on synthesized polyesters with the addition of reactive diluents curable at different temperatures.

Coating formation temperature, ^{0}C	Coating appearance;	Drawing resistance with a coefficient of 0.6	Film adhesion before sterilization, point;	Film adhesion before sterilization, normal tear, MPa	Coating impact strength, cm;	Film tensile strength, mm.
170	Transparent	Resist.	1	3.0	50	9.0
175	Transparent	Resist.	1	3.0	50	9.0
180	Transparent	Resist.	1	5.5	50	8.5
185	Transparent	Resist.	1	7.5	50	8.5
190	Transparent	Resist.	1	10.0	50	8.5
195	Transparent	Resist.	1	12.0	50	8.5

29309-92, also the adhesion after sterilization was evaluated, five cups batches (see table 6), it is clear that with a decrease in temperature from 185 to 170ºC sterilization resistance of coatings is reduced. So, during formation of coatings at a temperature of 170 – 180ºC, practically all cups have peeling of the coating. However, during formation of coatings at a temperature within 185-190ºC, coatings successfully pass these tests. It should be noted that an increase in temperature also causes an increase in adhesive strength. In our opinion, this is due to an increase in the frequency of crosslinking of the polymer network in combination with an increase in the proportion of glycide groups contributing to adhesion.

Discussion of the results

In the course of this work, the influence of reactive diluents on the formation of coatings based on unsaturated polyesters synthesized on the basis of neopentylglycol, terephthalic acid, phthalic and maleic anhydrides was studied. Derivatives of methacrylic acid and allyl alcohol were used as such reactive diluents. It is noted that the use

TABLE 6. Assessment of sterilization resistance of coatings based on the composition consisting of the synthesized polyester with an active diluent – glycidylmethacrylate, in the amount of 10% by weight, cured at different temperatures

Sample No.	Coating formation temperature, ^{0}C	Resistance to sterilization (visual)	Film adhesion after sterilization, point;	Film adhesion after sterilization, normal tear, MPa
	195	Resistant	1	10.5-11.5
1	170	Multiple rips	3	Less than 2.0
2	170	Multiple rips	3	Less than 2.0
3	170	Multiple rips	3	Less than 2.0
4	170	Multiple rips	3	Less than 2.0
5	170	Multiple rips	3	Less than 2.0
1	175	Multiple rips	3	Less than 2.0
2	175	Multiple rips	3	Less than 2.0
3	175	Multiple rips	3	Less than 2.0
4	175	Multiple rips	3	Less than 2.0
5	175	Multiple rips	3	Less than 2.0
1	180	Small rips	1	3.5
2	180	Small rips	2	3.0
3	180	Resistant	1	4.0
4	180	Small rips	2	3.0
5	180	Resistant	1	4.0
1	185	Resistant	1	3.5
2	185	Resistant	1	4.5
3	185	Resistant	1	4.0
4	185	Resistant	1	5.0
5	185	Resistant	1	4.5
1	190	Resistant	1	7.5
2	190	Resistant	1	7.0
3	190	Resistant	1	6.5
4	190	Resistant	1	6.5
5	190	Resistant	1	7.0

of derivatives of methacrylic acid, in particular, glycidylmethacrylate, improves physico-mechanical properties of coatings, primarily, the adhesion strength and operation and resistance to sterilization in modeling environments.

Conclusion

The results obtained allow us to give an answer to some theoretical aspects related to the laws of formation of coatings based on unsaturated polyesters in the presence of reactive diluents. It should be noted that can varnishes and enamels are used for production of a wide range of metal containers, while one of the most important requirements for coatings are adhesive strength and their resistance to sterilization in model environments. 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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