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Polyester Resins for Coating Cans with Improved Resistance to Stamping Operations: A View on Specific Properties

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ABSTRACT

Compositions containing epoxy diane oligomers make up a major of coatings applied to the insides of cans and other metal containers. Even though such materials allow producing coatings with good adhesion to metal substrates, with proper chemical resistance and elasticity, they have one major drawback, caused by the key component of diane epoxy resins, by the bisphenol A. The danger of this substance is that it has a negative effect on the human brain and the reproductive system, and sparks cancer. Therefore, such materials are I limited use. Composites based on polyester resins are a good alternative with good prospects. However, polyester coatings intended for cans and other packages have low resistance to sterilization, which is typically prior to a food canning process. The reason why this parameter is low is that given polymers contain a relatively high content of ester groups, which are characterized by low resistance to water, alkaline and acid agents. Such coatings can be improved in resistance by enriching the composition of their polymer macromolecules with unsaturated monomers that can homopolymerize when polyester compositions cure. These fragments are to create additional steric hindrance on diffusion for destructive ester groups and to ensure the endurance of coatings in general.

Keywords: polyester resins, canning varnishes, tinplate coating

INTRODUCTION

Containers for packing foodstuffs include cans made of white tinplate, and those of chrome-plated steel or aluminum sheets and plates. Such containers are routinely coated. The major purpose of these coatings is to prevent the contact with contents (food products) so that metal corrosion or any other effect of metal on the quality of food is eliminated [1]. The coating should not affect or damage the content by dissolving or migrating components of varnish material, fair enough. Therefore, requirements for can coatings are very high when it comes to elasticity, resistance to solvents and chemicals, as well as to toxic components that go in coating compositions [2].

Protective lacquers and varnishes for sheet metal packages are typically made of high-molecular weight epoxy and/or phenolic resins. With those, coating can imply the application of several layers, which is necessary if a high-quality corrosion protection is required along with the protection from critical deformations of metal sheet to guarantee a long shelf life [3]. All epoxy resins that are in work contain fragments of 4.4'-Isopropylidenediphenol (bisphenol A (BPA), diphenylolpropane), including simple 2.2-bis (4-hydroxyphenyl) propane bis (2.3-epoxypropyl) ether, and its homologues, known also as bisphenol-A-diglycidyl ester (BADGE).

Since the beginning of the XXI century, BPA and its derivatives were in the focus, especially their effect on the human body. In recent decades, this effect, more specifically the effect on the human endocrine system, was proven to be negative. In vitro, BADGE displays mutagenic and carcinogenic effects even in ultra-small amounts that migrated to packaged food from the coating [4].

The SpecialChem Company conducted a survey among experts in coating production about the possible alternatives to these materials. The results revealed that 36.2% of researchers viewed modifying of epoxy resins as

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a priority, meaning the replacement of BPA with other bisphenols like F and C bisphenols, or with various diglycidyl ethers, such as resorcinol diglycidyl ether, 1.4-Cyclohexanedimethanol diglycidyl ether, neopentyl glycol diglycidyl ether, 2-methyl-1.3-propanol diglycidyl ether and bis-epoxide obtained from 2.2.4.4-tetramethyl-1.3-cyclobutadione (TMCBDI). This will allow sticking to traditional epoxy compositions. The disadvantage of this strategy is related to toxicological evidences on bisphenols F and C, and to the availability of said diglycidyl esters, which are available in a limited range [5, 6].

Another part of researchers (28.7%) favored the production of canning paints and varnishes with polyester resins. With polyesters as the key binder, the range of opportunities in creating materials with necessary properties is broad [2]. Some authors describe materials from pure polyesters as those with high physical and mechanical properties [7, 8]. However, the application range of such compositions is narrowed to the covering of metal sections, known as coil coating, which does not imply the manufacture of containers for food. The list of disadvantages also includes the fact that they contain a significant amount of solvents (over 70%), which levels down their environmental friendliness of and increases the consumption of raw materials that go for coatings [8]. Besides, the use of heavy solvents means the eventual migration of those into the product to-be-packed, which negatively affects its quality.

At the same time, 20.5% of researchers favored favored the production of canning paints and varnishes with polyurethanes. Polyurethane (PUR) materials allow creating coatings with good decorative properties. With PUR materials, two major issues will arise – high cost and toxic character of diisocyanates. They can be minimized by combining chemical properties of polyurethanes with those of polyesters, which is a path to the minimum amount of diisocyanates in the resin.

BADGE-free roller coatings are described in some patents claiming the use of polyesters with blocked polyisocyanates in can coating [9]. Authors note high physical and mechanical properties of coatings based on such materials. However, when hot-dried, blocked polyisocyanates remove the blocking agent, which is butanone oxime or e-caprolactam. However, these agents do not meet the Health-Based Exposure Standard 2.3.3.97 2-00 *Maximum Permissible Quantities of Substances Released from Materials that are in Contact with Food* [10] and may partially remain in the coated layer and then migrate to what inside the container. Therefore, it is questionable whether to apply such coating systems to the inside of a food can.

In our opinion, the most beneficial path to environmentally friendly coatings is through materials based on polyester resins.

Polyester resins are cross-linked using various amine-containing products, which make the curing process formally close to that in compositions based on epoxy resins. Coatings based on such compositions are expected to have proper adhesion, flexibility, and resistance to drawing and bending.

Thus, some suggest using polyesters and polyether acrylates to exclude BADGEs and make coatings with good adhesive properties [11]. Some pioneered a method for making a water-borne BADGE-free polyester composition with high physical and mechanical properties, and acceptable resistance to sterilization in water [12]. However, both solutions are based on methanolized hexamethylene, which implies a potential migration of substances harmful to humans, such as methanol and formaldehyde. At this point, documents provide no data on such possibility.

Thus, epoxy and epoxy-phenolic materials used for coating tinplate are replaced by BPA-free polyester compositions. In papers devoted to the production of polyester materials, authors usually follow the path of varying their compositions (various cross-linkers plus polyester matrices). However, this route has limitations associated with the toxicity of most of these cross-linkers.

Therefore, approach introduced in this article to a target-specific change in the structure of a polyester molecule, which idea is to get a one-component composition, is unique.

This path is essential for practical applications (synthesizing polyesters for can coating in a technologically convenient way) and for science (contributing to the chapter on polyester resins) [13-16].

For the improvement of stamping resistance, polyesters can be enriched with unsaturated compounds — fatty acids. Fatty acids from vegetable oils and pure vegetable oils are widely used in the coating industry. Speaking of significant applications, they are used to synthesize the so-called alkyds, which a re-modified polyesters in essence [16, 17]. The disadvantage of such polymers is that they provide coatings, which surface membranes display low hardness and poor resistance to sterilization. Pure alkyds are not used in tinplate coating, but adducts based on them, alkyd-epoxy resins in particular, are [18].

These disadvantages are from a raft of ester groups in the structure of alkyds, including those that came with fatty acids. Therefore, the share of fatty acids should be small enough to prevent a jump in the fraction of ester groups and thereby avoid the problems with subsequent sterilization. On the other hand, non-saturated double bonds can homopolymerize in the presence of atmospheric oxygen, encouraging the formation of an additional polymer network along the unsaturated fragments, as well as the emergence of a steric effect.

When introducing mono-functional fatty acids, one should keep in mind that they are chain breakers, so their excess can lead to a decrease in the molecular weight of the polymer and have a negative effect on such properties as elasticity and stamping capacity.

Therefore, such fragments should be added in a strictly defined range.

In terms of structure, polyester resins for a can vary in average molecular weight, chain branching degree and the number of free functional groups (hydroxyl and carboxyl groups). At this point, molecular weight distribution is dependent upon the first two parameters.

Traditionally, industrial polyesters have an average molecular weight in the range of 800 to 4000, and branching degree in the range of f=2.01-2.5 [19, 20].

Depending on the molecular weight and the branching degree of a polyester chain, the hydroxyl number is usually between 50 and 150 mg KOH/g. Such a high concentration of hydroxyl groups is attributable to their role in polymer cross-linking and the fact that they provide the adhesion strength to various substrates.

Residual carboxyl groups that came from the condensation reaction usually define the acid number in the range from 1.0 to 30.0 mg KOH/g. When they do, they act as a condensation regulator and serve as a co-catalyst for the processes of condensation and coating.

The composition of structural units differs between industrial polyesters. Despite the existence of so many raw materials, these binders are typically made of those that guarantee optimal properties and are more cost-efficient and useful [21, 14].

Concerning the polycarboxylic acids, the choice turns next to phthalic acids and their derivatives, which are the key component of many polyesters. They are often combined with dicarboxylic acids, such as adipic and sebacic ones, to reduce the glass transition temperature and improve solubility. The most common polyethers are now the phthalic anhydride polyethers, due to a relatively low cost. However, colorful systems on their basis have a relatively low elasticity and low viscosity [15].

As for the cycloaliphatic polycarboxylic acids, one can note the hexahydrophthalic acid (or its anhydride), which is used if certain weatherability is required. With tetrahydrophthalic acid (or its anhydride), interlayer adhesion increases, but weatherability drops, so this acid usually goes into leveling systems or primers. Higher aliphatic dicarboxylic acids are more expensive than adipic and sebacic acids. Even though they improve some properties of a coating composition, such as adhesion and elasticity, better, these components are used rarely due to a high cost.

With fatty acids and their derivatives, coating compositions gain an increase in elasticity and better hydrocarbon solubility. On the one hand, double bonds are no good for weatherability of coatings that are made with such polyesters, but on the other hand, they enable coating by polymerization, if the corresponding unsaturated fragments are there in the structure of polyesters [17].

Speaking of diols, neopentyl glycol is the most attractive compound, as it does not project a strong plasticizing effect, and both of its side methyl groups provide polyester with good solubility [22]. Neopentyl glycol is often combined with a small amount of other diols, such as 1.6 hexanediol and hydroxypivalic acid neopentyl glycol ether. The use of neopentyl glycol is limited because it is more expensive that ethylene glycol and propylene glycol. However, last two glycols have a negative effect on solubility and does not allow obtaining systems resistant to water and aggressive media, but they have a strong plasticizing effect as a cherry on top. Polyesters with a high content of neo-structured diols, which side chains are longer than in neopentyl glycol (1.3-ethyl-butyl-propanediol, for example), are completely soluble in aromatic compounds and have wide compatibility. If the goal is to achieve a high glass transition temperature and coating hardness without an aromatic component, then dimethylolcyclohexane and hexahydrophthalic anhydride are to be chosen in combination with other structural units. In truth, such compositions are quite expensive as well.

Trimethylolpropane is usually used as a branched component in this group of polyesters [16]. This compound and other three primary hydroxyl groups are used instead of glycerin, which easily comes out and makes the coatings to yellow, among other things.

Other polyols carrying more than two functional groups are used much less frequently. In concept, branching may occur in reaction with polycarboxylic acid that has more than two functional groups, like trimellitic acid (or its anhydride). Polyesters with such a structure are quite rare, since they do not have unique advantages and require a lot of time and effort when produced.

METHODS

The synthesis was carried out in a typical reaction vessel. The process was guided by the acid number. The resulting polyesters were analyzed by the viscosity-average molecular weight, glass transition temperature, acid and hydroxyl numbers.

The properties of synthesized polyesters were assessed on coatings prepared by dissolution in a mixture of organic solvents. A cross-linker and surface additives were added until a working viscosity of 120-130 seconds, checked using aB3-4 viscometer. The mass fraction of nonvolatile substances was 50±3% by weight. Then, the coating was applied to electrolytic white tin-plate for cans until a dry film thickness of 6-8 g/m^2. A 15-minute curing was performed in a convection oven at a temperature of 195-200^{0}C.

First properties to assess were the decorative, physical and mechanical properties, such as:

— appearance of the coating;

— drawing quality (by ISO 1520);

— adhesion before sterilization (by GOST 15140; method 2[24]);

— coating strength at impact (by GOST 4765);

— coating strength under tensile stress (by GOST 29309).

The number of synthesis attempts for each polyester was different; the minimum number was three attempts in a series. The goal was to achieve a specifies acid number with an error of 10%. The basic composition to synthesize included:

— ethylene glycol;

— glycerin;

— etriol;

— diethylene glycol (DEG);

— neopentyl glycol (NPG);

— terephthalic acid (TFA);

— isophthalic acid;

— adipic acid (APA);

— sebacic acid (SA);

— phthalic anhydride;

— palm oil fatty acids;

— catalyst.

The ratio between carboxylic acid and hydroxy acid equivalents was equimolar.

In syntheses labeled DAG x or otherwise, "x" meant that this formulation contained diethylene glycol (DEG) in *x* amount (in moles).

Each synthesis was performed on 15 cans: 5 cans for each attempt.

An enlarged batch of cans (40 units) was made from three synthesized polyesters, according to the optimal formulation.

Photomicrographic images were taken using a digital microscope with 80X magnification.

In case of success, coatings were evaluated for resistance to sterilization by dipping a can in drinking water at a temperature of 120^{0}C for one hour, and for adhesion after sterilization (by GOST 5981, GOST 5717 and GOST 25749) [23].

RESULTS

The basic formula of choice was the composition for synthesizing polyethylene terephthalate (PET), with an equimolar ratio of carboxyl and hydroxyl groups. Since PET is a rigid-chain polymer, which has a negative effect on its solubility in organic solvents, elasticity and stamping capacity, the composition was later enriched with neopentyl glycol (NPG) and diethylene glycol (DEG). The phthalic anhydride was included as well to reduce the cost of the polymer.

Table 1 presents data on the properties of synthesized polyesters. **Table 2** presents the test data on coatings that were made from synthesized polymers.

Table 1. Properties of Synthesized Polyesters with Regard to Glycol Monomers

Synthesis Marking*	Molecular Weight		Acid Number, mg KOH/g**		Hydroxyl Number, mg KOH/g		Glass Transition Temperature, ^{0}C
	by calculation	viscosity-average	instant	final	by calculation	by analysis	
DEG 0.1	1728	1800	20	15	44.97	52	64
DEG 0.15	1582	1700	17	12	53.95	60	72
DEG 0.17	1474	1500	19	15	57.17	70	68
DEG 0.20	1138	1200	25	20	73.6	80	66
NPG 0.1	1728	1800	20	15	44.98	60	70
NPG 0.15	1581	1700	17	12	53.97	65	74
NPG 0.17	1408	1500	19	14	60.68	70	80
NPG 0.20	1138	1300	25	20	73.64	80	82
NPG 2.0	2240	2500	25	24	25.2	37.3	89

Note:

** Marking is attributed to the compound being added: DEG – diethylene glycol, NPG – neopentyl glycol.*

***instant, meaning theacid number at the end of synthesis; final, meaning the acid number of polyester in coating, equivalent to 100% polyester*

Table 2. Properties of Coatings from Synthesized Polyesters with Regard to Glycol Monomers

Synthesis Marking*	Non-Volatile Residue, % by weight	Viscosity	Appearance	Resistance to Drawing	Adhesion before Sterilization, points	Impact Strength, cm	Tensile Strength, mm	Resistance to Sterilization	Adhesion after Sterilization, points
Basic Formula	51.2	128	transparent	parts ripped off	1	50	8.5	removes completely	-
DEG 0.1	52.7	132	transparent	parts ripped off	1	50	7.5	multiple parts ripped off	3
DEG 0.15	47.9	139	transparent	parts ripped off	1	50	8.5	removes completely	-
DEG 0.17	50.7	133	transparent	parts ripped off	1	50	8.5	multiple parts ripped off	3
DEG 0.20	50.3	127	transparent	micro-cracks	1	50	9.0	few parts ripped off	3
NPG 0.1	49.0	123	transparent	micro-cracks	1	50	6.0	few parts ripped off	1
NPG 0.15	50.6	136	transparent	micro-cracks	1	50	5.5	few parts ripped off	1
NPG 0.17	52.8	125	transparent	micro-cracks	1	50	6.0	few parts ripped off	1
NPG 0.20	50.2	120	transparent	micro-cracks	1	50	5.5	few parts ripped off	1
NPG 2.0	48.7	128	transparent	few micro-cracks	1	50	5.5	few parts ripped off	1

Presented data show that almost all synthesized polyesters allow creating homogeneous transparent coatings with good adhesion that withstand a blow up to 50 cm.

However, synthesized polyesters did not pass the sterilization test.

With NPG, coatings have lower resistance to stretching. Moreover, film strength decreases from 8.5 mm to 5.5-6.0 mm. When drawn, surface of the covering has micro-cracks.

However, coatings based on polyesters containing neopentyl glycol had small partial segments ripped off during sterilization, while coatings made by following the basic formula were mechanically removed from the test cans completely after sterilization.

With DEG, coated film became more resistant to stretching with a high, which is 9.0 mm, at 0.2 mol concentration of DEG. When added in this concentration, DEG improved the drawing resistance so that only few micro-cracks were observed. However, this compound does not improve the resistance to sterilization. Even in a 0.2 mol concentration, it gives the result, which is similar to that given by neopentyl glycol.

The complete lack of resistance to sterilization in the case when ethylene and diethylene glycol are used is probably caused by the hydrolysis of ester bonds in a polyester. The neopentyl glycol, however, appears to create a steric hindrance on this reaction.

Table 3. Properties of Synthesized Polyesters with Regard to Phthalic Acid Fragments

Synthesis Marking*	Molecular Weight		Acid Number, mg KOH/g**		Hydroxyl Number, mg KOH/g		Glass Transition Temperature, ^{0}C
	by calculation	viscosity-average	instant	final	by calculation	by analysis	
TFA 0.75	3733	4300	15	15	15.14	20	94
TFA0.8	3294	3500	17	15	17.16	23	84
TFA0.9	2667	3000	21	18	21.2	25	87
TFA0.95	2435	2700	23	20	23.22	32	96
TFA1.0	2240	2700	25	25	25.23	33	98
TFA1.1	2545	2300	22	18	22.21	28	98
TFA1.2	2667	2800	21	15	21.4	26	98
TFA0.0	2240	2200	25	25	25.23	34	65

Note:

** Marking is attributed to the compound being added: TFA – terephthalic acid.*

***instant, meaning the acid number at the end of synthesis; final, meaning the acid number of polyester in coating, equivalent to 100% polyester*

Table 4. Properties of Coatings from Synthesized Polyesters with Regard to Phthalic Acid Fragments

Synthesis Marking	Non-Volatile Residue, % by weight	Viscosity	Appearance	Resistance to Drawing	Adhesion before Sterilization, points	Impact Strength, cm	Tensile Strength, mm	Resistance to Sterilization	Adhesion after Sterilization, points
Basic Formula	51.2	128	transparent	parts ripped off	1	50	8.5	removes completely	-
TFA 0.75	48.7	121	transparent	micro-cracks	1	50	8.0	few parts ripped off	2
TFA 0.8	50.7	139	transparent	micro-cracks	1	50	7.5	few parts ripped off	3
TFA 0.9	51.8	127	cloudy	micro-cracks	1	50	7.5	few parts ripped off	2
TFA 0.95	50.4	139	cloudy	micro-cracks	1	50	7.5	few parts ripped off	2
TFA 1.0	51.3	135	cloudy	micro-cracks	1	50	7.5	few parts ripped off	3
TFA 1.1	51.3	135	cloudy	micro-cracks	1	50	7.5	few parts ripped off	3
TFA 1.2	51.3	135	cloudy	micro-cracks	1	50	7.5	few parts ripped off	3
TFA 0.0	48.9	128	transparent	multiple parts ripped off	2	40	5.5	removes completely	-

To check this assumption, polyester was synthesized with neopentyl glycol alone (synthesis marking NPG 2.0). It turned out that this solution gives the best drawing resistance. Only few micro-cracks were detected after sterilization, and that they can only be seen under a microscope. Stretching resistance is not that good as in the case of ethylene glycol. In our opinion, this fact can be explained by different types of deformation processes that take place in polyester films. On the top of that, neopentyl glycol alone gives better sterilization resistance than it does in combination with ethylene glycol.

An interesting pattern is given by data on the glass transition temperature (**Table 1**). The highs were detected when neopentyl glycol was used alone. In this case, molecular weight of synthesized polyester reached the maximum and was about 2500.

Thus, ethylene glycol and diethylene glycol are recommended to elimination, so that the composition was based on neopentyl glycol alone.

The isomers of phthalic acid have a different effect on the properties of polyesters. When it comes to application, the most interesting compounds are para-phthalic and orthophthalic (as an anhydride) acids, as para-phthalic acid increases the degree of polyester crystallinity, which guarantees a more dense packing of polymeric macromolecules and increases chemical resistance. Phthalic anhydride is one of the cheapest carboxyl-containing products, which favorably affects the cost of production.

Data in **Table 3** shows with an increase in the terephthalic acid, glass transition temperature increases as well, indicating an increase in the chain stiffness. However, in a polyester, terephthalic acid does not change the resistance to physical and mechanical stress, no matter the amount added (**Table 4**).

Table 5. Properties of Synthesized Polyesters with Regard to Dicarboxylic Acid Fragments

Synthesis Marking*	Molecular Weight		Acid Number, mg KOH/g**		Hydroxyl Number, mg KOH/g		Glass Transition Temperature, ^{0}C
	by calculation	viscosity-average	instant	final	by calculation	by analysis	
SA 0.65	991	1100	15	10	98.09	110	78
SA 0.75	1199	1300	18	13	75.55	90	78
SA 0.85	1526	1600	20	15	53.58	70	82
SA 0.95	1972	2000	23	18	34.01	50	85
SA 1.0	2240	2500	25	20	25.23	40	86
APA 0.65	989	1100	15	10	98.32	110	82
APA 0.75	1223	1300	17	12	74.74	90	78
APA 0.85	1566	1600	19	14	52.69	70	74
APA 0.95	1970	2100	23	18	34.05	50	72
APA 1.00	2240	2500	25	20	25.23	40	69
APA 1.05	4402	3400	18	18	7.61	5.9	65
APA 1.10	3833	3500	25	25	4.46	3.2	65

Note:

** Marking is attributed to the compound being added: APA – adipic acid, SA – sebacic acid;*

***instant, meaning the acid number at the end of synthesis; final, meaning the acid number of polyester in coating, equivalent to 100% polyester*

Table 6. Properties of Coatings from Synthesized Polyesters with Regard toDicarboxylic Acid Fragments

Synthesis Marking*	Non-Volatile Residue, % by weight	Viscosity	Appearance	Resistance to Drawing	Adhesion before Sterilization, points	Impact Strength, cm	Tensile Strength, mm	Resistance to Sterilization	Adhesion after Sterilization, points
Basic Formula	51.2	128	transparent	parts ripped off	1	50	8.5	removes completely	-
APA 0.75	51.0	130	transparent	micro-cracks	1	50	8.5	tiny parts ripped off	3
APA 0.85	52.6	126	transparent	micro-cracks	1	50	7.5	tiny parts ripped off	2
APA 0.95	52.1	135	transparent	micro-cracks	1	50	7.5	tiny parts ripped off	2
APA 1.00	50.7	123	transparent	few micro-cracks	1	50	7.5	test passed	1
APA 1.05	48.3	138	transparent	micro-cracks	1	50	7.5	tiny parts ripped off	2
APA 1.10	47.5	142	transparent	micro-cracks	1	50	7.5	tiny parts ripped off	2

Note:

** Marking is attributed to the compound being added: APA – adipic acid*

With terephthalic acid in concentration of more than 0.9 moles, resulting coatings lose their decorative appearance – they become cloudy and gave white sediment at storage. This happens because terephthalic acid undergoes a reaction and partially falls out of the polymer.

With the exclusion of terephthalic acid from the polyester (TFA-0.0), physical and mechanical properties of coatings from it experienced a negative change. They also did not pass the sterilization test. Thus, phthalic anhydride is likely to induce the formation of a super-rigid structure.

Since pure terephthalic acid is not appropriate to use when synthesizing polyethers for tinplates, due to its high melting point (above 450^{0}C), other types of carboxyl-containing components are required.

Thus, phthalic anhydride should also be removed from the polyester formula.

Adipic and sebacic acids were chosen to assess the effect of carboxylic acids on the polyether properties.

With sebacic acid, synthesized coatings gave white sediment in all cases. In our opinion, this sediment came form unreacted particles of sebacic acid, which is unacceptable for canning varnishes and lacquers. Therefore, samples containing sebacic acid were removed from further trials.

With adipic acid, glass transition temperature decreased, probably due to an increase in the flexibility of polyether macromolecules (**Table 5**). This change was expected to improve the resistance of coatings to drawing and stretching. Performed trials show that adipic acid does not improve the resistance of polyester coatings to drawing, stretching and sterilization (**Table 6**).

Table 7. Sterilization Resistance of Enlarged Batch of Cans from Synthesized Polyesters Containing Adipic and Terephthalic Acids by Technical Specifications 10.244.003-90 (Industrial Standard 10-84-87)

Can Number	Coating Adhesion before Sterilization, points	Resistance to Sterilization	Coating Adhesion after Sterilization, points
1	1	test passed	1
2	1	tiny parts ripped off	1
3	1	test passed	1
4	1	test passed	1
5	1	test passed	1
6	1	test passed	1
7	1	test passed	1
8	1	test passed	1
9	1	test passed	1
10	1	test passed	1
11	1	test passed	1
12	1	test passed	1
13	1	test passed	1
14	1	tiny parts ripped off	1
15	1	test passed	1
16	1	test passed	1
17	1	test passed	1
18	1	test passed	1
19	1	test passed	1
20	1	test passed	1
21	1	test passed	1
22	1	test passed	1
23	1	tiny parts ripped off	1
24	1	test passed	1
25	1	test passed	1
26	1	test passed	1
27	1	test passed	1
28	1	test passed	1
29	1	test passed	1
30	1	tiny parts ripped off	1
31	1	tiny parts ripped off	1
32	1	test passed	1
33	1	test passed	1
34	1	test passed	1
35	1	test passed	1
36	1	test passed	1
37	1	test passed	1
38	1	test passed	1
39	1	test passed	1
40	1	test passed	1

Note: adipic and terephthalic acids are in 1.0 to 1.0 proportion

Five out of forty cans, coated with a coating composition made of polyester synthesized by formula containing adipic and terephthalic acids in proportion of 1.0 to 1.0 (synthesis marking APA 0.1), did pass the sterilization test, retaining the adhesion, which they had before sterilization (**Table 7**).

In our opinion, such results indicate that even though adipic acid increases the flexibility of polyether macromolecules, a three-dimensional network with considerable stresses at its nodes still forms in the coating. When these nodes are exposed to mechanical deformation, the network breaks. This results in micro-cracks and micro-fractures, which get larger when cans are sterilized (**Figure 1**). With too many of them, the coating just layers off.

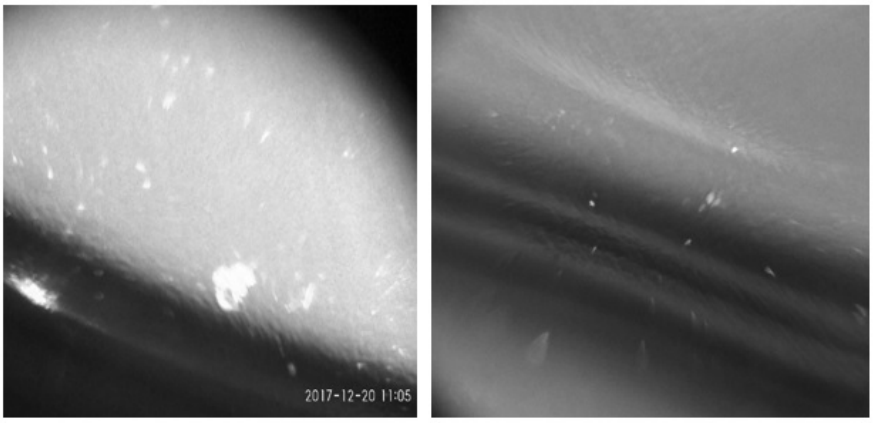

Figure 1. Photomicrographic View of Fractured (a) and Ripped off (b) Segmentson a Film Membrane with Dicarboxylic Acid Fragments after Sterilization by Technical Specifications 10.244.003-90 (Industrial Standard 10-84-87)

Table 8. Properties of Synthesized Polyesters with Regard to Fatty Acid Fragments

Synthesis Marking*	Molecular Weight		Acid Number, mg KOH/g**		Hydroxyl Number, mg KOH/g		Glass Transition Temperature, ^{0}C
	by calculation	viscosity-average	instant	final	by calculation	by analysis	
SOFA 0.10	4953	4500	22	18	11.51	12.4	66
SOFA 0.15	7879	7600	9	12	7.02	5.3	69
SOFA 0.25	5728	5300	17	16	9.62	7.4	63
SOFA 0.35	3630	3700	22	17	15.22	20	58
SOFA 0.45	2231	2300	23	18	24.89	40	56
SOFA 0.50	gelling effect						

Note:

** Marking is attributed to the compound being added: SOFA – sunflower oil fatty acids;*

***instant, meaning the acid number at the end of synthesis; final, meaning the acid number of polyester in coating, equivalent to 100% polyester*

Therefore, polyester formulas hould include agents that increase elasticity, for example – fatty acids.

Trials that implied a significant amount of fatty acids added to the polyester (over 0.25 moles) displayed a jump in viscosity and foaming in the reaction mass, up to complete solidification. This phenomenon, the so-called "gelling" is associated with the occurrence of side reactions on the double bond – with the oxidative polymerization at prolonged subjection to synthesis temperature.

By synthesizing in a stream of nitrogen, oxidative polymerization was reduced. At the same time, a significant amount of fatty acid (up to 0.45 moles) was introduced. Greater amounts are not advisable, since gelling effect was observed even in a stream of nitrogen.

With fatty acid, glass transition temperature of the polyester was significantly reduced (**Table 8**), indicating a potential increase in the elasticity of the polymer.

As expected, it turned out that the use of fatty acid improves the resistance of coating to drawing and stretching (**Table 9**). Coatings that passed all the tests displayed an even film membrane under the microscope, without any defects (**Figure 2**).

Table 9. Properties of Coatings from Synthesized Polyesters with Regard to Fatty Acid Fragments

Synthesis Marking	Non-Volatile Residue, % by weight	Viscosity	Appearance	Resistance to Drawing	Adhesion before Sterilization, points	Impact Strength, cm	Tensile Strength, mm	Resistance to Sterilization	Adhesion after Sterilization, points
SOFA 0.10	51.6	121	transparent	test passed	1	50	8.5	removes completely	-
SOFA 0.15	52.9	124	transparent	test passed	1	50	8.5	removes completely	-
SOFA 0.20	52.6	126	transparent	test passed	1	50	8.5	removes completely	-
SOFA 0.25	51.9	125	transparent	test passed	1	50	8.5	removes completely	-
SOFA 0.35	53.0	123	transparent	test passed	1	50	8.5	removes completely	-
SOFA 0.45	52.8	120	transparent	test passed	1	50	8.5	removes completely	-
Phospholipid from Vegetable Oil	47.1	179	transparent	test passed	1	50	9.0	parts ripped off along the top of the can	2

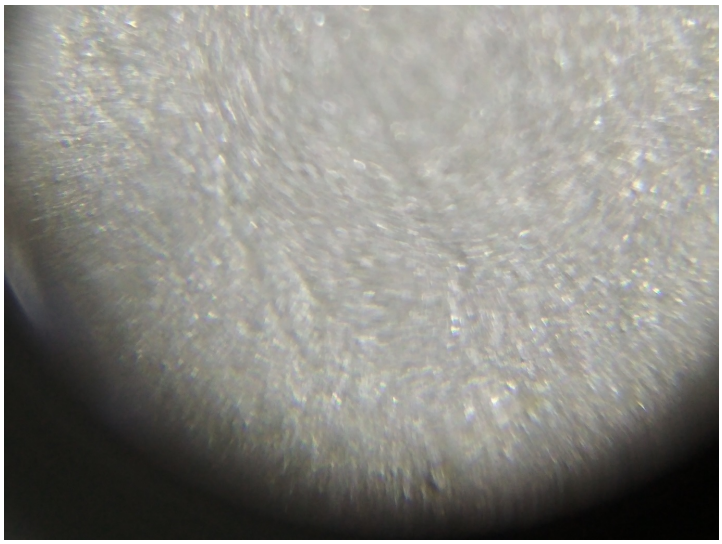

Figure 2. Photomicrographic View of Coating with Fragments of Sunflower Oil Fatty Acid: Drawing Resistance by GOST 29309-92

A batch of 40 sterilized cans had no visual defects of coating (**Figure 3**), which suggests that fatty acid fragments are advisable to add to eliminate the hydrolysis of ester groups during sterilization. Since we cannot change the activity and chemical nature of the ester group, we suggest adding monomer fragments to the polyester, which are responsible for tactical position of side substitutes relative to the main polymer chain.

Figure 3. Cans Coated with Coating Composition from Synthesized Polyester Containing Fragments of Sunflower Oil Fatty Acid: View after Sterilization in Drinking Water

DISCUSSION

This article was about the possibility of making a target-specific change in the monomeric composition of polyester resins in order to manipulate with their properties.

The use of basic laws of polycondensation in combination with modified ones (the introduction of target mono-functional compounds) allows creating coatings with required properties from one-component polyester materials.

Although modification of polymer molecules is a common technique for changing their properties, this is the first attempt to regulate the composition of polyesters used in the manufacture of food cans, which has quite specific requirements for the final product.

Despite the fact that the chemistry of polyester synthesis is reduced to the interaction of a hydroxyl-containing component with a carboxyl-containing one, which patterns are described in the literature, actual process is influenced not only by the ratio of carboxyl equivalent to the hydroxyl one, or by the type and concentration of a catalyst, but also by the functional groups. This is true even for linear polycondensation.

When making a target-specific change in the structure, data on the effect of a monomer fragment in a polyester macromolecule will allow predicting how the qualitative and quantitative composition of the initial monomer mixture will affect physico-mechanical (glass transition temperature, elasticity, scratch resistance) and physico-chemical properties (wetting, liquidity, adhesion) and targeted properties (ability to cure under certain conditions and resistance to sterilization in model environments).

CONCLUSIONS

Research results allow us not only to answer some theoretical aspects of polyester synthesis, but also to consider the features of technology scaling at transferring laboratory data to experimental and industrial installations.

Canning varnishes and enamels are used to coat a wide range of metal containers, which have fundamentally different requirements imposed on them.

For example, a drawn can must have a good drawability, so related coatings should have good elasticity and adhesion. A built-up can must be resistant to stamping operations resistance, so its coat must be resistant to impact and bending, naturally.

The insides of containers must be covered with materials that are resistant to model environments, while their outsides must look good, be resistant to scratching, etc.

Cans are made of ferrous and non-ferrous metals, which are treated using different methods, namely:

— white hot dipped tinplate;

— white electrolytic tinplate;

— black tinplate;

— anodized aluminum tinplate;

— food-grade aluminum tinplate with chromate-phosphate coating;
etc.

Naturally, different substrates will give different wetting and bottling properties. This should be taken into account when creating polyester systems.

This research will allow introducing a new safe product to the market of canning varnishes and enamels. This product will improve the efficiency of food canning technology by making cans safer for production and storage (by excluding toxic and carcinogenic substances).

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