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Polymer stoppers: Quality of alcohol beverages during storage

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Abstract:
Polymer stoppers are gaining popularity over traditional corks. However, their quality level remains understudied, as does their effect on commercial alcoholic beverages. This research featured the quality and safety indicators of polymer stoppers. The research objective was to assess their potential impact on the quality and safety of alcoholic drinks during storage.
The study focused on six types of polymer stoppers that differed in manufacturer, price, and material. Such aspects as appearance, geometry, impermeability, sensory profile, and polymer dust were determined based on State Standard 32626-2014. Toxic substances were assessed by gas chromatography while the migration of substances from the stopper surface was studied using direct microscopy. Sample preparation protocol followed Technical Regulation of Customs Union 005/2011 and State Standard 32626-2014.
Certain stoppers, mainly from the low-cost segment, failed to meet the impermeability requirements, especially in case of hot-process bottling. The experiment revealed such toxic and hazardous substances as dibutyl and dioctyl phthalates, acetone, ethyl acetate, hexane, heptane, methanol, propyl, butyl, and isobutyl. They penetrated into the model environment and deteriorated the sensory properties of the alcoholic beverages. The acceptable level of methanol migration was exceeded by ≥ 10 times. The concentration of propyl alcohol reached 0.435 mg/L, with its acceptable level being 0.100 mg/L. The concentration of ethyl acetate was 20 times as high as the standard.
The research confirmed phthalate migration from polymer stoppers into alcoholic beverages during storage. Their migration rate and concentration in the finished product correlated with the strength of the beverage and storage temperature. Apparently, winemakers should apply stricter sanitary, quality, and safety standards to the stoppers they use to bottle their produce.

Keywords: Polymer materials, bottling, corks, alcohol industry, safety, toxic elements, dioctyl phthalate, dimethyl phthalate

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INTRODUCTION

The wine and the stopper have been inseparable throughout human history. The stopper has been a key element of wine preservation during storage, from the epoch of amphorae to modern glass bottles. The earliest stoppers were made from any available materials, such as wood, bamboo, etc. Natural cork stoppers appeared in the IX century. Eventually, their production technology became as mechanized as that of glass bottles.

However, the cork tree and, subsequently, the cork itself are vulnerable to pests and various microorganisms. Their waste products may spoil the wine. Mold-induced polychlorophenols and polychloroanisoles cause a moldy taint and a number of other wine faults, even at low doses [1, 2]. Moreover, the cork tree has become a depletable resource that needs protection. To support the market for natural wine stoppers, the alcohol industry has introduced alternative variants. Polymer stoppers (Fig. 1) are a functional analogue to traditional corks. They are made of synthetic polymers treated with silicone or other similar substances. Since they entered the market in the late XX century, polymer stoppers have remained a popular cork alternative.

The current share of polymer stoppers is 16–20% of the global market for wine stoppers [3]. They are made by casting or coextrusion from food packaging polymers.

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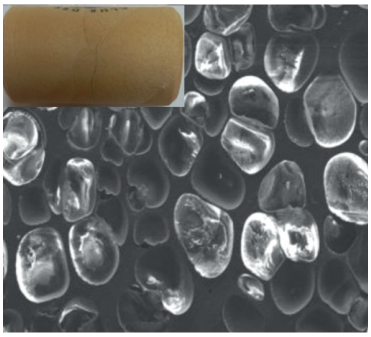


Figure 1 Polymer cork structure, scanning electron microscopy

Casting, or injection molding, involves pouring a mix of thermoplastic elastomers (styrene-butadiene-styrene and styrene-ethylene/butadiene-styrene) into a special mold cavity. Coextrusion is a two-step process. First, high-density polyethylene and talc are mixed, melted, and extruded as a long foam cylinder. Second, the resulting stopper is thermally bonded to the outer flexible shell made of thermoplastic elastomer based on high-density polyethylene [4, 5]. To satisfy consumers, synthetic stoppers are designed to imitate the properties of natural cork, but, unlike real cork, polymer stoppers are microbiologically inert [6].

Once wine is bottled, sealed, and labelled, it acquires a complex set of attributes that give it some extra concept: bottled wine is much more than the sensory properties of the beverage itself. Winemakers extend the range of brands and styles by designing new types of packaging: it is the bottle shape, glass color, label, and stopper that make a wine brand unique.

The type of stopper affects consumer perception of the wine, making the external attributes no less important and attractive than the internal ones, e.g., taste, bouquet, and overall wine quality [7]. In this case, consumers tend to exaggerate the quality properties of wine sealed with a natural cork.

A particular stopper can add wine immediate value by improving its appearance: consumers believe that it reflects the quality of the wine, which affects their purchasing decision [7]. Although most polymer stoppers are scientifically proved safe, consumers still prefer natural ones, presuming that natural cork preserves and even improves the quality of wine during storage. However, the quality of the cork itself remains beyond their concern, probably, as a result of inertia and resistance to change and innovation [8].

Other problems associated with cork stoppers include wine oxidation, discoloration, leakage, crumbling, etc. A natural cork stopper often falls apart during opening. Using low-quality natural cork eventually results in lost revenue, as consumers start to avoid the brand, attributing the poor quality of the product to the winemaker rather than the cork [9]. Consumer perception appears to be the main marketing factor for each type of wine stoppers.

Impermeability is the main function of stoppers, i.e., preventing leakage during storage. Permeability for oxygen is another important factor that affects the sensory profile of wine, including its color [10, 11].

Stoppers and their effect on wine aging have recently become a popular research issue [12–14]. However, it was Louis Pasteur who discovered that oxygen was both *a friend and a foe* to wine quality due to its ability to change the sensory properties and appearance of wine during aging [15]. Oxygen exposure improves the taste, preserves the color, and reduces the astringency of red wine [14, 16]. However, too much oxygen spoils white wine: it darkens, ages too fast, and acquires unwanted flavor and smell [12, 17]. Similarly, too little oxygen during aging promotes the formation of undesirable low molecular weight sulfur compounds, e.g., hydrogen sulfide or hydrosulfides. It suppresses some flavor compounds, as well as develops silicon and rubbery taints, also known as reductive aromas (reductive notes) [12, 17, 18].

Recent research [17, 19] shows that packaging materials, including stoppers, can have a negative impact on the appearance and other quality indicators of alcoholic beverages. Its effect on the quality and safety of wine is a matter of vigorous discussion [20]. Some experts insist that natural cork remains the best material while others claim that polymer analogues are better in preserving wine quality [21, 22].

Yet, polymer stoppers require a complex and labor-intensive production technology that employs materials of various nature, not to mention auxiliary agents. Moreover, polymer stoppers can lead to contamination with microplastics and plasticizers.

Phthalates are much more than a mere plasticizer responsible for flexibility and elasticity: they are high-boiling substances that provide polymers with resistance to thermal and thermal-oxidative degradation, water, and ultraviolet radiation. An effective material with high elasticity and wear resistance may contain as much plasticizer (phthalate) as the polymer itself [23]. Most industrial phthalates are used to plasticize polyvinyl chloride. The type of *o*-phthalic acid ester and its amount in polyvinyl chloride depend on the application of the final polymer product.

Phthalates are organic compounds, derivatives of benzene-1,2-dicarboxylic acid. They are formed when phthalic anhydride interacts with aromatic or aliphatic alcohols with 0 (1)-13 carbon atoms. The substituents can be symmetrical or asymmetrical. All phthalates are colorless low-polar oily high-boiling liquids that are highly soluble in most organic solvents and poorly soluble or even insoluble in water [24, 25].

Individual esters of *o*-phthalic acid are known for their pathogenic action. Modern phthalate studies focus on just a few of them, i.e., diethyl phthalate (DEP), dimethyl phthalate (DMP), dibutyl phthalate (DBP), and bis(2-ethylhexyl) phthalate (DEHP). Most researchers that used a number of homologues to study phthalate toxicology report their toxic effect as inversely proportional to the molecular weight of the ester radical [26].

Many countries have food safety requirements for phthalates. However, the existing standards seldom coincide for each individual homologue:

– EU Commission Regulation 10/2011 of January 14, 2011, on plastic materials and articles intended to come into contact with food fails to mention the acceptable amounts for diethyl phthalate and dimethyl phthalate;

– Russian Sanitary/Hygienic Rules and Standards 1.2.3685-21 on safety of environmental factors for people give the maximum allowable concentrations for diethyl phthalate, dibutyl phthalate, and bis(2-ethylhexyl) phthalate in an inverse correlation with concentration values of 3.0, 0.2, and 0.008 mg/L, respectively;

– European Directive 2008/105/CE of December 16, 2008, sets the maximum allowable concentration of bis(2-ethylhexyl) phthalate in water as 0.0013 mg/L;

– The USA have no restrictions on the acceptable content of diethyl phthalate and dimethyl phthalate in food products (Public Law 110-314-AUG. 14, 2008).

Russian food safety standards stipulate the content of such phthalates as dibutyl phthalate and dioctyl phthalate in polymer stoppers. For instance, dioctyl phthalate is banned from model environments that come into contact with bottle stoppers.

Dibutyl phthalate and dioctyl phthalate are orthophthalic acid esters. They have four hydrogen bond acceptors and bond with reducing agents.

The current scientific interest in food-package phthalates is due to their high pathogenic activity [27]. The content of phthalates is strictly regulated by Technical Regulations of Customs Union 055/2011 and Russian Sanitary/Hygienic Rules and Standards 1.2.3.685-21.

The Japanese Chemical Management Center and the US National Institute of Standards and Technology classify dibutyl phthalate and dioctyl phthalate as reproductive toxins and skin sensitizers that also disrupt the endocrine system and cause the so-called phthalate syndrome [28, 29]. However, these substances exhibit such toxicity only when heated [30]. Apparently, the storage conditions of wine sealed with a polymer stopper should exclude any chance of temperature increase.

Many research institutes study the kinetics of phthalate migration due to the wide application range of phthalate-containing materials and the high lability of phthalate molecules.

The rate at which plasticizer migrates from polymer depends on a number of physical factors. Such diffusion-related factors as temperature, pressure, humidity, nature, and solvent volume can be controlled while others cannot, e.g., polymer composition, nature, and content of plasticizer, distribution density of plasticizer in polymer, interaction with other additives, etc.

Lazakovich *et al.* [31] reported that wine can be contaminated with phthalates as early as at the production stage. In addition, time also contributes to contamination, i.e., the longer the production process, the higher the contamination risk.

The rate with which phthalates enter water-alcohol solutions depends on the alcohol concentration. The rate of natural extraction depends not so much on the alcohol content in the model as on the water content and the type of phthalate. In addition, the migration rate of phthalates into ethanol directly depends on temperature increase, which makes phthalate more soluble and mobile in supramolecular structures of the polymer (Fig. 2).

The migration rate increases together with the volume fraction of ethyl alcohol as the volume of water goes down. The extraction intensifies when the concentration exceeds 30% or the temperature goes beyond 20°C.

Russian winemaking industry is facing an acute shortage of wine stoppers because natural cork and most exported synthetic materials have fallen under sanctions.

The First Russian Winemaking Forum was organized by the Roscongress Foundation and the Federal Self-Regulatory Organization of Winegrowers and Winemakers of Russia in Moscow in November 2022. There it was announced that the capacity of the Russian market for alternative stoppers through 2033 would amount to 49 billion rubles (Fig. 3). As a result, the production of polymer wine stoppers is expected to grow.

Despite all these problems, the safety and quality assessment of polymer stoppers fall within the framework of the requirements established by the Eurasian Economic Union in the Technical Regulations of the Customs Union 005/2011 for safe food packaging and State Standard 32626-2014 that introduces general specifications for polymer stoppers.

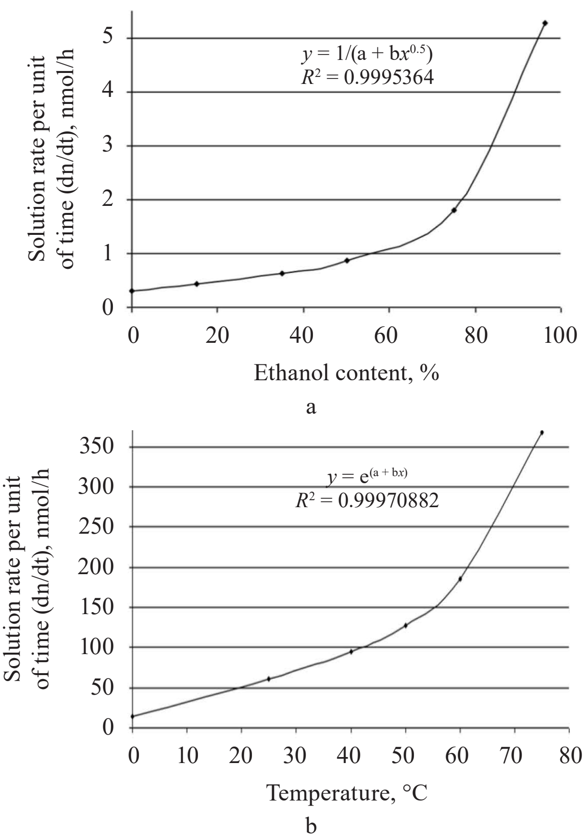
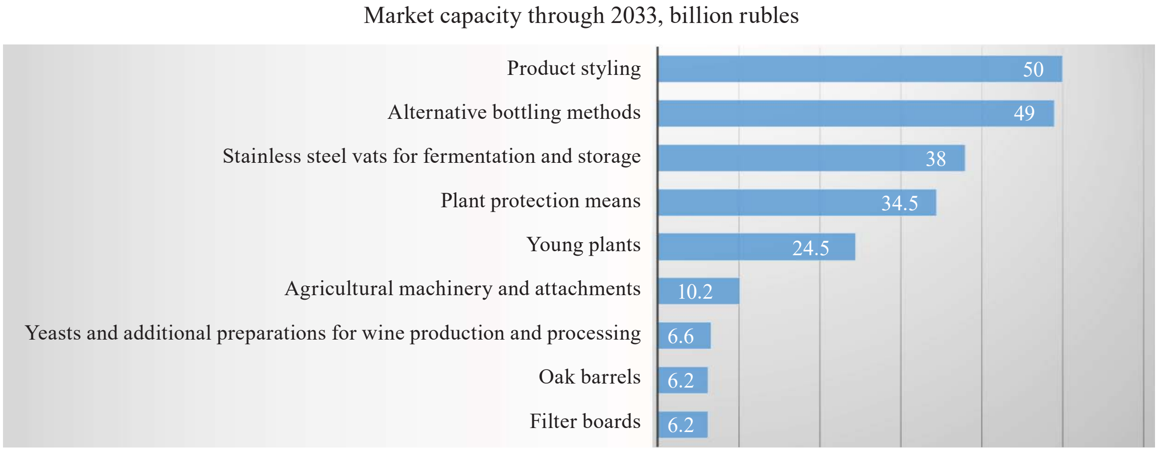


Figure 2 Migration rate of dibutyl phthalate from polyvinyl chloride throughout 7 h depending on ethyl concentration (a) and temperature (b)



From the presentation of the General Director of JSC MOE VINO Arsen Karapetyan within the framework of the topic "Science, agriculture, and industry for the development of winemaking in Russia": https://xn--80aea0d.xn--p1ai/20221125/231909.html

Figure 3 Wine stopper market through 2033 as announced at the plenary session of The First Russian Winemaking Forum 2022

In Technical Regulations of the Customs Union 005/2011, safety is provided by a set of requirements for the materials that contact with food. These requirements cover sanitation, hygiene, impermeability, chemical inertness, safe opening, and physical and mechanical indicators. The sanitary and hygienic safety indicators for polymer stoppers in the food industry include the content of formaldehyde, ethyl acetate, hexane, heptane, acetone, styrene, methyl, propyl, isopropyl, butyl, isobutyl, and phthalates. The Eurasian Economic Union (EAEU) specifies permissible levels of their migration into the model environment. The list of phthalates to be controlled includes dioctyl phthalate and dibutyl while the presence of dibutyl phthalate in model environments is not allowed.

In terms of physical and mechanical properties and chemical inertness, polymer stoppers must provide impermeability under standard operating conditions and withstand internal pressure if they are intended for sparkling wines. In addition, the amount of polymer dust is strictly standardized. State Standard 32626-2014 also specifies the requirements for appearance, shape, and sensory profile.

This research assessed effects of polymer stoppers on the quality and safety of alcoholic beverages on the domestic market.

STUDY OBJECTS AND METHODS

The experiment involved 27 samples of polymer stoppers available on the Russian domestic market (Table 1).

The stoppers were classified by the production method (casting or coextrusion) and market value. The low-cost cast stoppers were ≤ 10 rubles per piece; the medium-price cast stoppers were ≥ 10 rubles per piece. Coextruded medium-cost stoppers were 20–50 rubles per piece while those of premium level were ≥ 50 rubles per piece (price per one piece may vary within 30%, depending on the batch volume). The final price classification consisted of three types: low, medium, and premium. The classification also included such extra features of production and appearance as color. In addition, the research covered some new types of T-shape cast polymer stoppers (Fig. 4).

Cognac and grape vodka were provided by winemakers to establish effects of polymer stoppers on the quality of these alcoholic beverages.

The appearance of the stoppers was assessed visually, without magnifying, by comparing them with the description in standards State Standard 32626-214 and 34257-2017.

The dimensions were checked with State Standard 32626-2014 by direct measurement with a 0.05 mm caliper (State Standard 166-89, ISO 3599-76). All the measurements were carried out in triplicate with error assessment.

The impermeability tests followed State Standard 32626-2014, Art. 9.5. The glass bottles were filled with the product to the nominal volume and sealed with the test stopper, 10 pieces for each sample group. After that, the bottles spent 48 h in a horizontal position on filter

Table 1 Types of polymer stoppers

<table>
<tr><td colspan="27">Type and price</td></tr>
<tr><td colspan="3" rowspan="2">Cast stopper for sparkling wine</td><td colspan="24">Still wines</td></tr>
<tr><td colspan="3">Cast stopper, low-cost</td><td colspan="3">Cast stopper, medium-cost</td><td colspan="3">Painted cast stopper, medium-cost</td><td colspan="9">Coextruded stopper, premium</td><td colspan="6">Coextruded stopper, medium-cost</td></tr>
<tr><td colspan="27">Sample</td></tr>
<tr><td>1</td><td>2</td><td>3</td><td>1</td><td>2</td><td>3</td><td>1</td><td>2</td><td>3</td><td>1</td><td>2</td><td>3</td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td><td>7</td><td>8</td><td>9</td><td>1</td><td>2</td><td>3</td><td>4</td><td>5</td><td>6</td></tr>
</table>

a b c d

Figure 4 T-shape polymer stoppers: (a) wooden flange, (b) wood-covered flange, (c) and (d) goldish and blue metal-covered flange

paper. The packaging was considered impermeable if the filter paper demonstrated no trace of liquid.

The amount of polymer dust was determined for six stoppers per each group using the standard methods described in State Standard 32626-2014, Art. 9.11.

The sensory profile was defined by tasting the water-alcohol extracts that had contacted with the experimental stopper samples. The panelists were recruited from the Winemaking Research Center, North-Caucasian Federal Scientific Center for Horticulture, Viticulture, and Winemaking.

The high-precision equipment tests were carried out at the Shared Use Center and the Testing Laboratory, North-Caucasian Federal Scientific Center for Horticulture, Viticulture, and Winemaking. The mass concentrations in the model environments were determined by gas chromatography in line with State Standard 34174-2017 for ethyl acetate, hexane, heptane, acetone, and styrene, as well as methyl, propyl, isopropyl, butyl, and isobutyl. The method involved a gas chromatographic analysis of the equilibrium vapor phase using a vapor dozer on two parallel-connected capillary columns and two flame ionization detectors. The quantitative analysis relied on the absolute calibration method, with the arithmetic mean of two parallel measurements as the final result. The content of formaldehyde in the model medium was determined by gas chromatography in line with State Standard 33446-2015. The method was based on the reaction between formaldehyde and 2,4-dinitrophenylhydrazine in an acidic medium. The resulting 2,4-dinitrophenylhydrazone of formaldehyde was extracted with toluene, and the toluene extract underwent chromatography on a device with an electron capture detector. The final result was a mean concentration value by two parallel calculations. The migration of dioctyl phthalate and dibutyl phthalate was studied in line with State Standard 33451-2015 by gas chromatography with an electron capture detector, as well as by measuring the concentrations in the model environment by toluene extraction. The final result was the arithmetic mean of two parallel measurements.

The potential migration of polymer and other dusts from the stopper surface into the model environment and finished products was studied by subjecting the sediment to microscopy. The sediment was isolated by centrifuging the water-alcohol extracts and finished products. The microscopy involved an Olympus microscope (Japan) and a webcam.

The samples were prepared in line with Technical Regulation of Customs Union 005/2011, Appendix 2. A 20% water-alcohol solution with 2% citric acid served as the model solution of wine. A 40% water-alcohol solution simulated grape vodkas and cognacs.

RESULTS AND DISCUSSION

We tested the samples for compliance with the requirements of State Standard 32626-2014, which covers appearance, geometry, impermeability, smell, flavor, color, and transparency changes, as well as the amount of polymer dust.

Foreign smells in the model environment proved to be the main non-compliance for most samples. Almost all samples (90–100%) of cast stoppers in all price segments introduced undesired smells into the model solution. This phenomenon resulted in rejecting 10–20% of coextruded stoppers of premium cost; however, the medium-cost coextruded stoppers of the same type did not give the final product any foreign smell.

The low-cost cast stoppers and the coextruded medium-cost stoppers violated the impermeability indicator. The proportion of rejected samples was 6–10% for the cast stoppers and 1–3% for the coextruded stoppers.

Other parameters demonstrated no violations.

Figures 5 and 6 visualize permeability that occurred after 10 min in the reclined position (Fig. 5). When the bottle was re-verticalized, some liquid accumulated on the stopper surface in the neck area (Fig. 6). In addition to product loss, such faulty stoppers may trigger bacterial development in the bottle neck, and microorganisms may eventually enter the finished product during storage.

The hot-process bottling test, when the beverage was heated to 40°C before bottling, revealed a two-fold increase in permeability, and the share of non-compliant

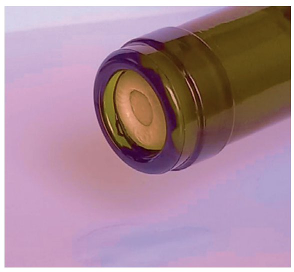


Figure 5 A permeable stopper

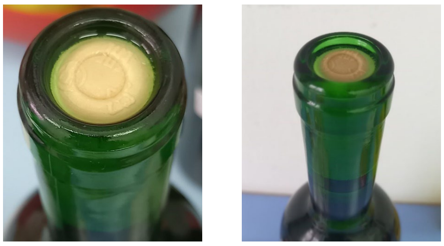
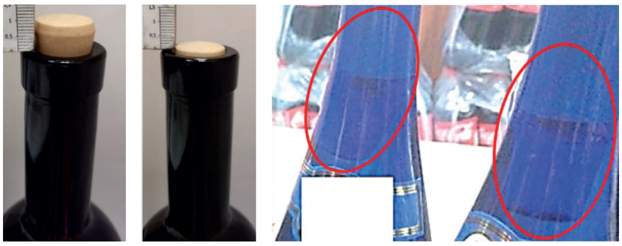
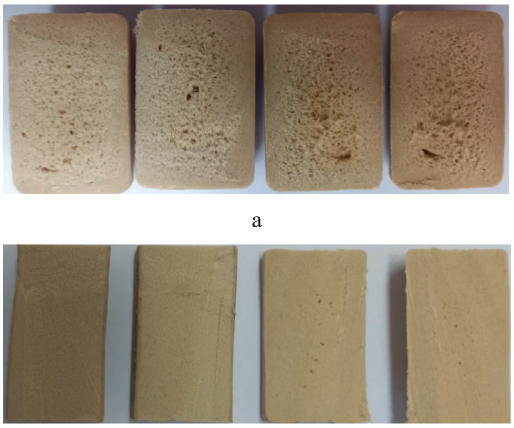


Figure 6 A faulty stopper



a b c

Figure 7 Permeability during hot-process bottling: (a) and (b) the stopper is sliding out, (c) the stopper is falling inside (the photos were taken in a retail chain shop)



a

b

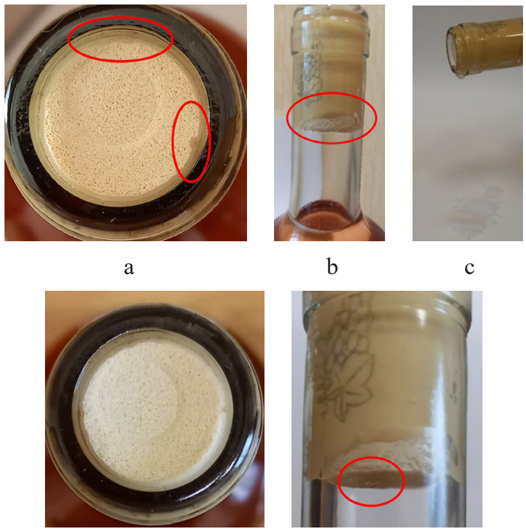
Figure 8 Internal structure of stopper samples: (a) faulty stoppers, (b) good-quality stoppers

stoppers reached 20%. In addition, the stoppers could partially slide down the bottle neck (Figs. 7a and b) or even fall inside completely (Fig. 7c). Yet, the accompanying documents for the cast stopper allowed for hot-process bottling.

During the cut test, the rejected samples demonstrated a non-uniform porous structure in the middle, which got denser at the periphery (Fig. 8a). The stoppers of the same type and quality that met the impermeability requirements had a uniform internal structure (Fig. 8b).

Probably, the low impermeability index resulted from poor technological standards.

Figure 9 shows a coextruded medium-cost stopper in a bottle that was withdrawn from the retail network for permeability. The bottle neck was subjected to visual in-



a b c

d e

Figure 9 Bottles withdrawn from the retail chain due to permeability: (a) the end of a coextruded stopper in the bottle neck with visible leakage, (b) horizontal leakage, (c) a loose stopper, (d) reverse leakage from the middle of the stopper to its lower end, and (e) leakage along the entire central part length

spection after removing the heat-shrink capsule. The end surface of the stopper was intact, but it was loose at the circumference and some part of the side length (Figs. 9a and b). When reclined, the bottle immediately started leaking (Fig. 9c). When returned to the vertical position, the liquid accumulated in the bottle neck above the stopper (Fig. 9d). Unlike the cast stoppers, the coextruded ones resulted in the leakage not only at the points of contact with the bottle neck, but also along the entire length of the central part, as evidenced by the accumulation of liquid on the bottom end surface of the stopper (Fig. 9e). Apparently, the porous structure of the coextruded stopper did not guarantee impermeability as a result of procedural violation.

A set of safety tests (Technical Regulations of the Customs Union 005/2011) indicated various quantities of the substances under analysis in the model environments, depending on the type and quality of the stopper. Figures 10–14 show the mean values for mass concentrations for each substance and stopper type. The widest range and the largest quantity of toxic substances belonged to the low-cost cast samples intended for still wine. They contained 0.795–0.877 mg/L of acetone, 1.998–2.470 mg/L methyl alcohol, and 1.030–1.230 mg/L dioctyl phthalate. These substances are toxic and may cause irreversible defects in the wine.

At these concentrations, acetone gives wine a synthetic flavor. Also, it reacts with various wine components, thus boosting oxidation. Dioctyl phthalate also enhances synthetic or chemical taints, as well as develops amorphous inclusions that destroy the commercial appearance. Red wines are especially at risk since they contain phenolic components that bond with cork phthalates.

The premium coextruded stoppers also demonstrated a high migration rate of unwanted substances into the wine. These samples had the highest acetone content across all the stopper types (1.549 mg/L). The methyl alcohol content reached 2.082 mg/L. Therefore, premium polymer stoppers do not guarantee the wine quality.

The medium-cost and premium coextruded stoppers also increased the concentration of ethyl acetate in the model environment: 0.918–2.972 and ≤ 0.698 mg/L, respectively.

The premium coextruded stoppers also demonstrated an active dioctyl phthalate migration (1.412 mg/L). The concentration was 0.873–0.952 mg/L for the sparkling wine cast stoppers and 1.030–1.230 mg/L for still wine stoppers. In the model environments that contacted with medium-cost coextruded corks, the dioctyl phthalate contration stayed below 0.1 mg/L (Fig. 11). Unlike other substances, the level of dioctyl phthalate corresponded with the standard established by EAEU Technical Regulations of Customs Union 055/2011, Appendix 1 (≤ 2000 mg/L).

For instance, the amount of propyl alcohol (Fig. 12) that migrated from the stopper into the model environment was exceeded several times in almost all samples, reaching 0.168–0.435 mg/L, while the standard concentration is ≤ 0.100 mg/L. The cast samples for sparkling wine (0.054 mg/L) and the medium-cost stoppers for still wine (0.097 mg/L) were the only exceptions.

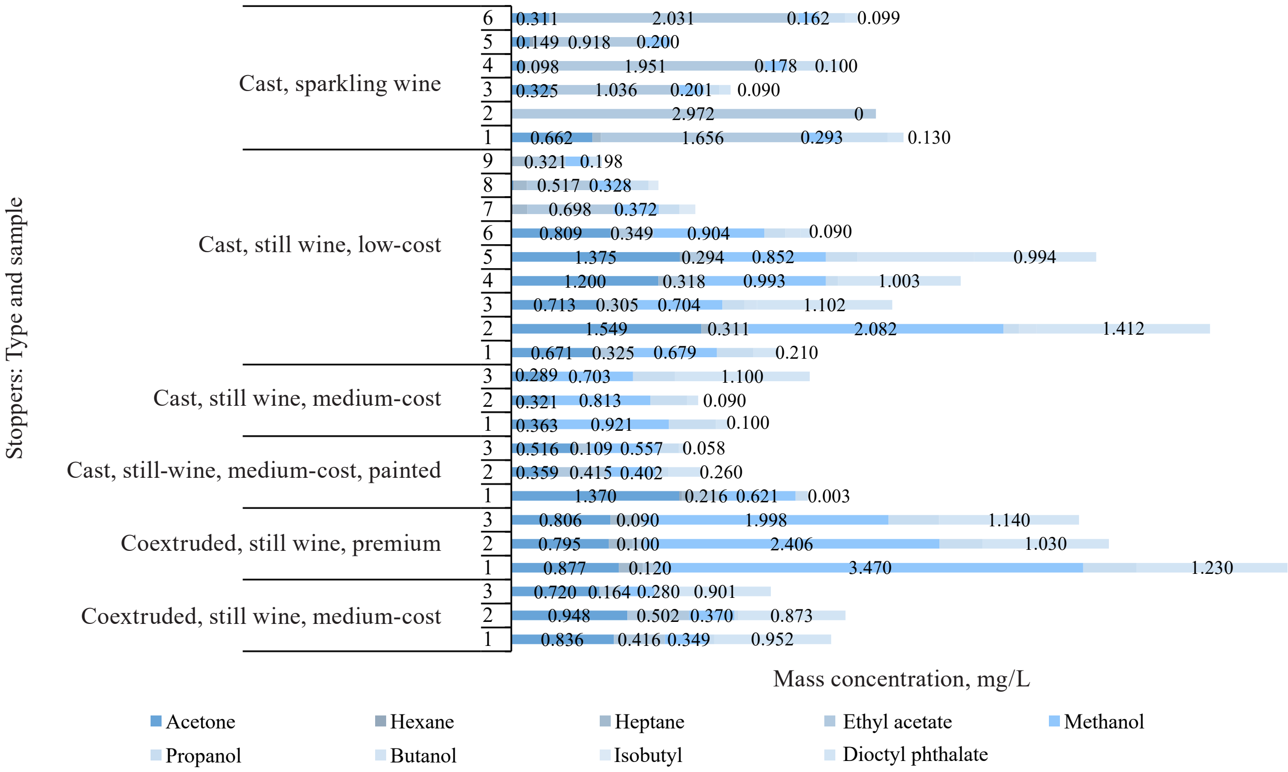


Figure 10 Mass concentration of substances released into the solution from various types of stoppers

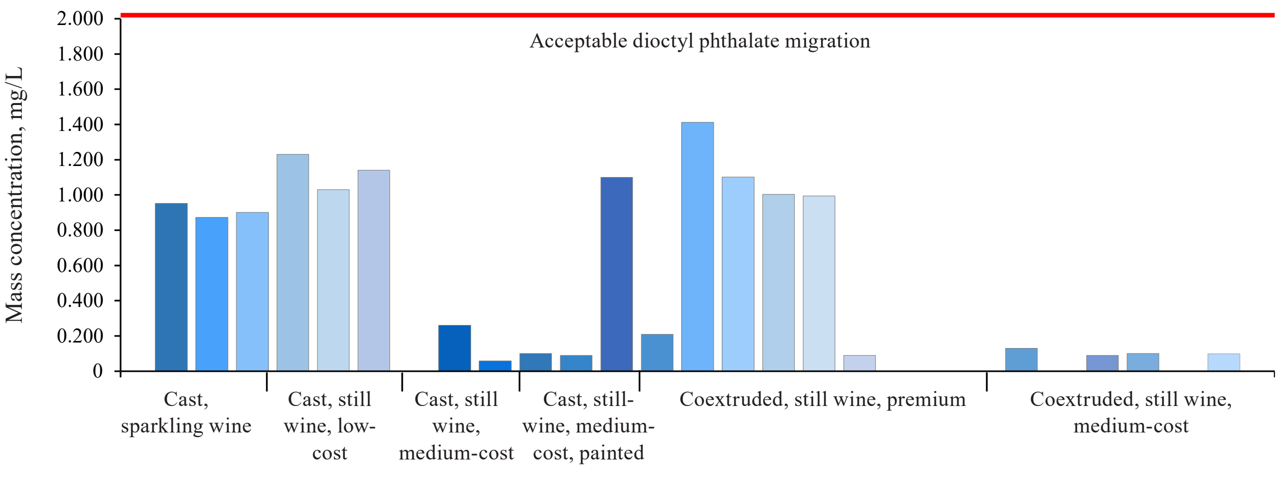


Figure 11 Dioctyl phthalate migration into model environments from various types of stoppers

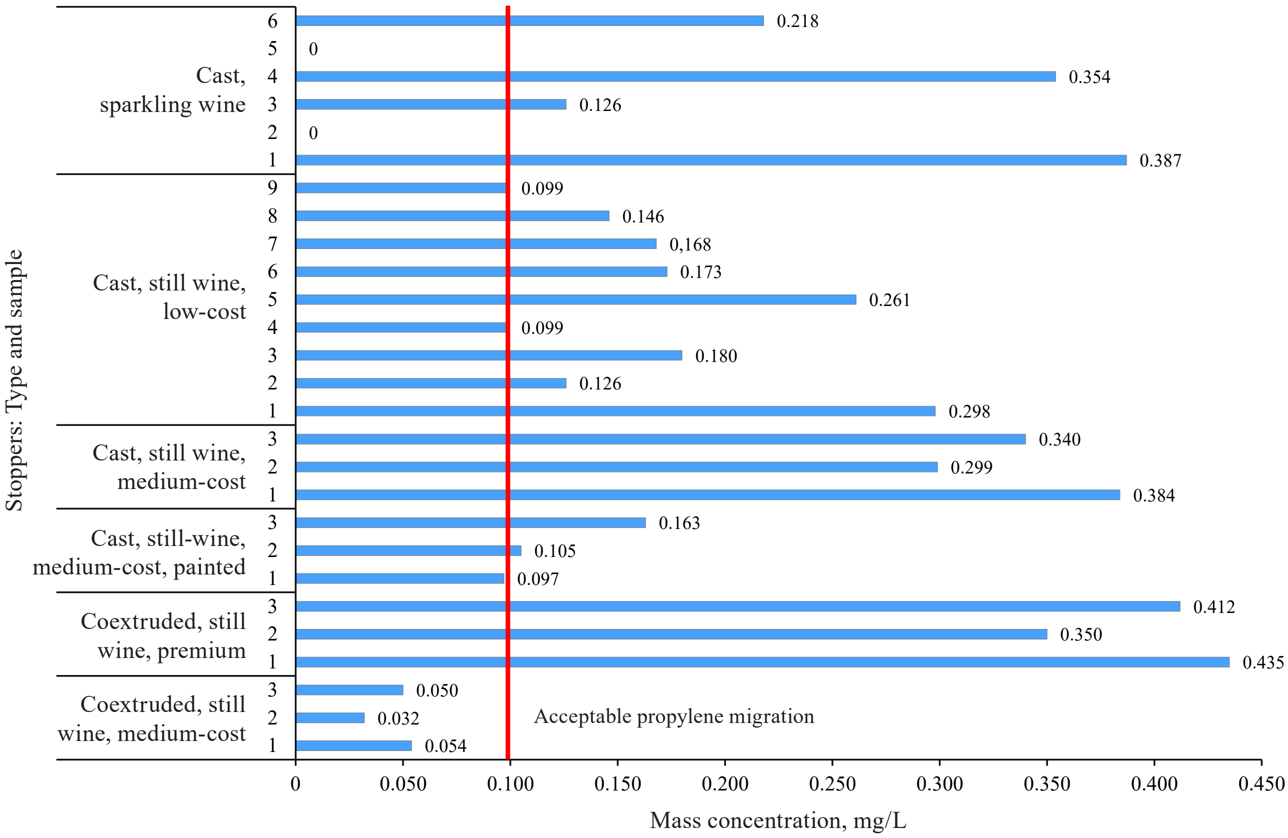


Figure 12 Propyl alcohol migration into model environments from various types of stoppers

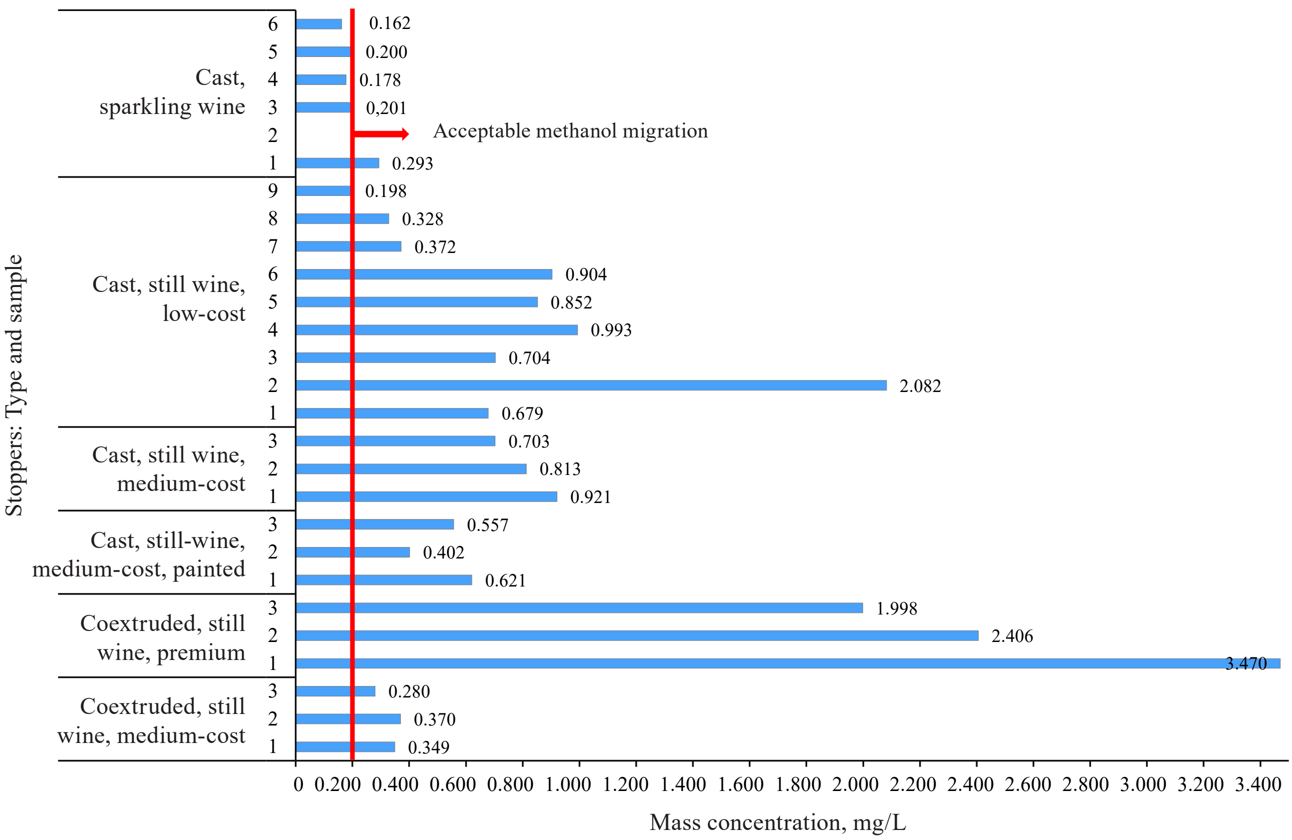


Figure 13 Methyl alcohol migration into model environments from various types of stoppers

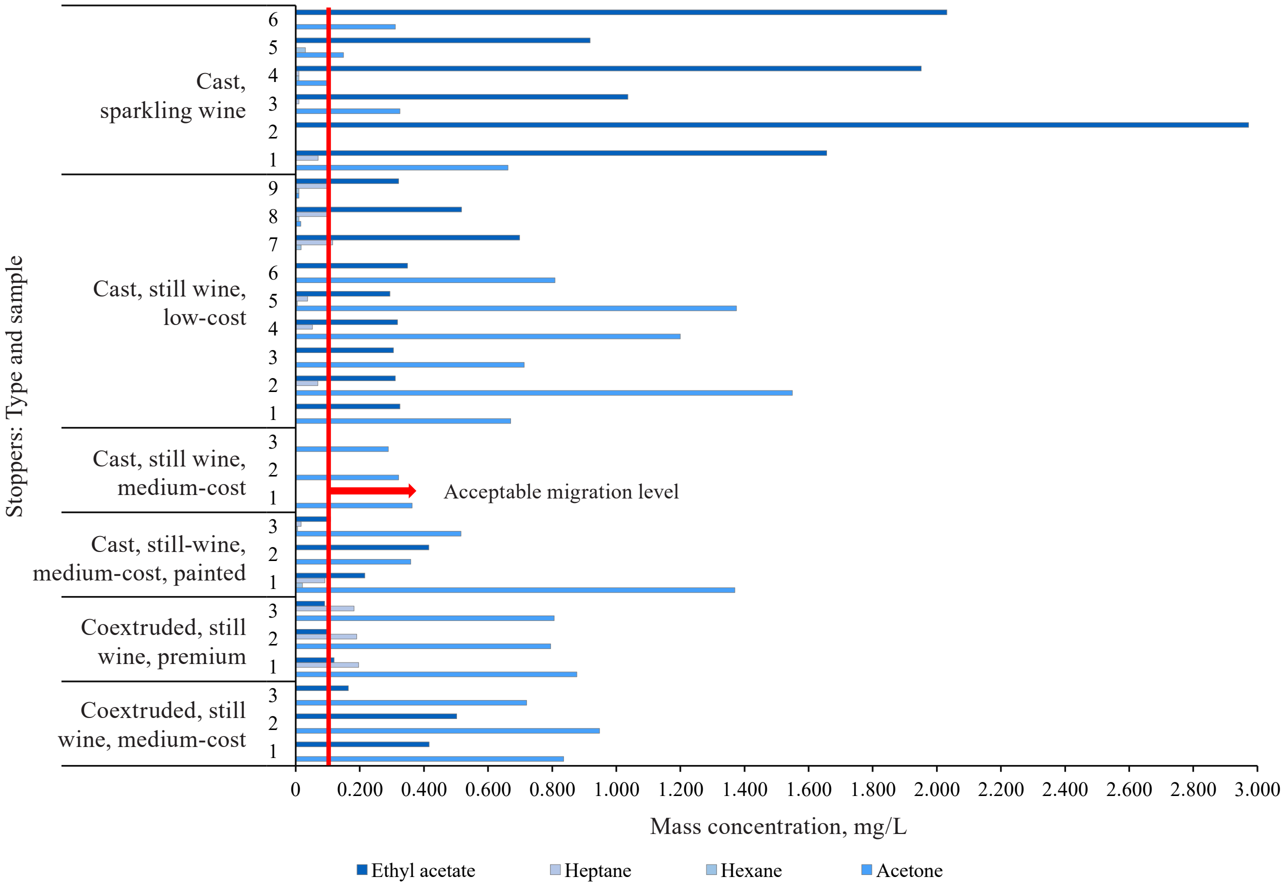


Figure 14 Mass concentration of substances released into the solution from various types of stoppers

The methyl alcohol migration far exceeded the standard (≤ 0.200 mg/L) (Fig. 13). The methanol level in the low-cost cast stoppers intended for still wine was by more than a tenfold higher (2.470 mg/L). The still wine premium coextruded stopper also extended a large amount of methyl alcohol into the model environment (2.082 mg/L).

Methanol is a common toxic pollutant that spoils alcoholic beverages. In distilled alcoholic drinks, the limits of methanol content are established in the regulatory documents for finished products (State Standards 31732-2014, 31728-2014, 31763-2012, 31493-2012, 55458-2013, 55459-2013, and 55461-2013). For example, the Interstate Standards for cognac and cognac distillates stipulate the mass concentration of methyl alcohol as ≤ 1.0 g/L; in wine distillates and wine alcohol, it is 2.0 g/L. In grape vodka, grape distillate, and grape alcohol, the national standards for methanol concentration are the same, i.e., ≤ 2.0 g/L.

Thus, the migration of methanol from the stopper increases its concentration in the drink, which may classify the product as hazardous when it is already in storage or on the shop shelves. Moreover, further storage increases methanol migration into the environment and, eventually, the toxicity of the drink.

Only some samples of premium coextruded stoppers demonstrated signs of butyl and isobutyl migration. Samples 7 and 8 were positive for isobutyl alcohol migration (0.08 and 0.13 mg/L, respectively). Samples 2, 3, 5, and 6 received 0.101–0.950 mg/L of butyl alcohol from of the same stopper type. Sample 5 violated the acceptable butanol migration level, i.e., ≤ 0.5 mg/L.

Butyl and isobutyl alcohols are always present in wine because they are secondary products of alcoholic fermentation. However, additional exposure to these alcohols violates the physical and chemical balance in the wine system, which has developed during production. It encourages butyl and isobutyl alcohols to react, and the wine esterifies in the bottle, resulting in unpleasant sharp alcoholic smell after opening.

Ethyl acetate was detected in large quantities in almost all the samples, except the painted medium-cost cast stopper for still wine (Fig. 14). This indicator was exceeded by more than a tenfold and reached 2.972 mg/L in the coextruded medium-cost stoppers. The premium coextruded stoppers rendered 0.294–0.698 mg/L of ethyl acetate into the solution, which also exceeded the threshold value of ≤ 0.100 mg/L. The low and medium-cost cast stoppers demonstrated a slight excess while no excess was detected for low-price samples 2 and 3. Ethyl acetate migration from the cast stoppers was 0.164–0.502 mg/L for sparkling wine, 0.09–0.12 mg/L for the low-cost cast stoppers for still wine, and 0.109–0.415 mg/L for the medium-cost cast corks.

Ethyl acetate is a potential source of unpleasant taint in alcoholic beverages [32]. It is the most common ester in wines that changes its native sensory profile. Ethyl acetate migration from the stopper also affects the wine quality.

The content of heptane that exceeded the acceptable level of 0.100 mg/L was observed in the low-cost cast stoppers for still wine (0.182–0.196 mg/L) and the premium coextruded stoppers (0.115 and 0.102 mg/L in samples 7 and 8, respectively).

An insignificant amount of hexane that fell within the norm of ≤ 0.1 mg/L was detected in the model environments that contacted with the medium-cost cast stoppers for still wine (0.021 mg/L in sample 1; 0.006 mg/L in sample 3), the premium coextruded stoppers (0.01–0.017 mg/L), and the medium-cost coextruded stoppers (0.01–0.03 mg/L).

The acetone concentration exceeded the standard of 0.100 mg/L in almost all the samples and ranged from 0.149 to1.549 mg/L, namely 0.720–0.948 mg/L in the cast stoppers for sparkling wine, 0.795–0.877 mg/L in the low-cost cast corks for still wine, and 0.359–1.370 mg/L in the medium-cost cast stoppers for still wine. The lowest concentration belonged to the painted stoppers (0.289–0.363 mg/L). The solution that contacted with medium-cost coextruded sample 2 contained no acetone while other samples of the same group contained 0.098–0.662 mg/L of acetone. A similar situation was observed for the solutions that contacted with the premium coextruded stoppers. For example, sample 7 contained no acetone whereas sample 2 demonstrated the highest acetone content across the similar samples (1.549 mg/L).

The painted medium-cost cast stoppers for still wine promoted only acetone migration (0.289–0.363 mg/L) whereas ethyl acetate, heptane, and hexane were totally absent from the model solutions.

When swallowed, acetone is absorbed rather quickly, but the pharmacokinetics and the metabolic pathway depend on the dose. Although acetone is neither genotoxic nor mutagenic, it enhances the toxicity of other organic compounds [33].

Dibutyl phthalate and formaldehyde did not migrate into the model solutions.

These results clearly demonstrate that polymer stoppers affect the safety of alcoholic beverages. Moreover, in this research, neither type nor price correlated with the migration rate of toxic substances into the liquid environment.

When the abovementioned chemical components enter the finished products, they intensify the oxidation processes and subsequently reduce or entirely spoil the quality of the drink by changing their appearance and other sensory properties.

As synthetic polymer stoppers contact with reactive components in wine, their surface gets damaged, and the resulting substances migrate into the wine. Further reactions lead to formation of new compounds. Oxidation and sorption are the most active reactions triggered by polymer stopper components. The resulting opaqueness and foreign inclusions spoil the commercial appearance. Other consequences include poor sensory profile and safety violation.

The standards for commercial wine products are practically the same as those for all food products. However, alcoholic beverages contain a lot of ethanol, organic acids, and flavoring agents. As a result, they are subject to much stricter quality control. The primary quality assessment begins with a visual inspection for compliance with legislative and regulatory standards.

In line with State Standards P 55458-2013 and 31732-2014, bottled wine products must be transparent and free of foreign inclusions or sediment. Otherwise, the products are rejected and withdrawn from circulation for violation of cosmetic standards.

Phthalate migration depends on their solubility in water-alcohol solutions. Its rate directly depends on the chemical composition of the model environment and the ambient temperature during storage. Bottled alcoholic beverages with ≥ 30% ethyl by volume sealed with polymer stoppers must be stored at temperatures below 20°C.

The three-star cognac sample sealed with a capped polymer stopper (Fig. 15) was rejected for foreign inclusions (Fig. 16): small particles clustered on its surface, which did not correspond with the standard appearance for this type of alcoholic drink.

A detailed examination of the unopened bottle (Fig. 17) revealed droplets on the surface of the stopper. When the

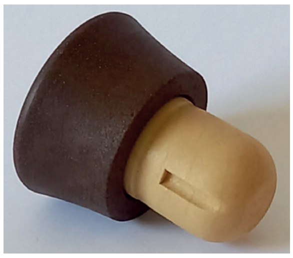


Figure 15 Capped polymer stopper

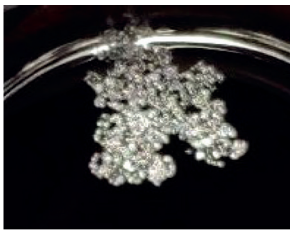


Figure 16 Foreign inclusions on cognac surface, 100× magnification

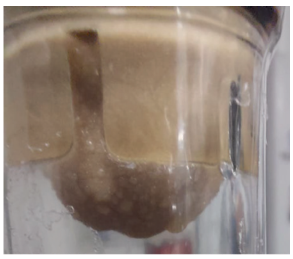


Figure 17 Stopper surface

bottle was tilted, the droplets flowed down the neck into the cognac. Presumably, it happened because the plasticizer protruded onto the stopper surface as a result of poor manufacturing protocol.

Microscopy was performed to study the droplets collected from the stopper surface and the inclusions sampled from the cognac surface. Figure 18 shows the microscopic images of the polymer stopper (a–c) and foreign inclusions on the cognac surface (d).

The foreign inclusions were of different shapes, i.e., plates, scales, and clusters. The inclusions on the surface of the stopper looked similar to those on the surface of the cognac. Logically, the commercial appearance of the cognac had been spoiled by the faulty stopper.

Phthalates have a high sorption capacity in relation to various classes of compounds in alcoholic beverages, especially those with a benzene ring [34]. Polymers have a well-developed spatial structure and a large specific surface area that serves as a platform for chemical interactions. For instance, Fig. 18d shows the accumulation of cognac tannins on the peripheral surface of the inclusions.

A model experiment test made it possible to confirm the role of the polymer stopper in wine quality degradation. The stopper samples were exposed to model solutions that simulated grape vodkas and cognacs. The stoppers were extracted from cognac bottles, rinsed with the abovementioned model solutions, microscoped for cleanliness, and applied to bottles with a water-alcohol solution similar to the model environment. To accelerate the extraction process, the bottles were stored upside down for 72 h to provide continuous contact between the solution and the stopper under normal environmental conditions (t = 20 ± 2°C). Then, the bottles were returned to the vertical position to test the drop on the stopper surface (Fig. 19). The model solutions demonstrated inclusions similar to those in Fig. 18, which were caused by synthetic components that had migrated there from the stopper.

Polymer compounds are known to smoke when burning. Depending on the composition, the flame is red-blue or black. A burning test was conducted to define the nature of the sediment. The inclusion components were washed from cognac and burned on a spatula: they indeed emitted smoke, and the flame was red-blue, with occasional black shades. The test proved the presence of polymer stopper components in the foreign inclusions that made the cognac non-saleable.

To validate the result, the cognac samples were tested for phthalates using the standard method described in State Standard 33451-2015. Sample 1 that featured 17-month-old cognac contained 0.18 mg/L of dibutyl phthalate and 0.01 mg/L of dioctyl phthalate. Sample 2 of 12-month-old cognac contained 0.17 mg/L of dibutyl phthalate and 0.03 mg/L of dioctyl phthalate.

Another sample featured a glass bottle of grape vodka sealed with a T-shape polymer stopper. It was obtained from a finished product warehouse and contained tiny scale-like inclusions.

The substances isolated from this product were compared with the components that migrated into the model environment from new stoppers of the same type. The microscope images showed similar inclusions of various sizes in amorphous clusters. Apparently, they resulted from the surface treatment of stoppers and/or polymer inclusions, possibly phthalates (Fig. 20).

To confirm that the identified inclusions belonged to the polymer stoppers, a similar test was conducted for some new polymer stoppers available on the domestic market (Fig. 4).

Microscope images of the sediments showed that the inclusions developed from the substances that migrated

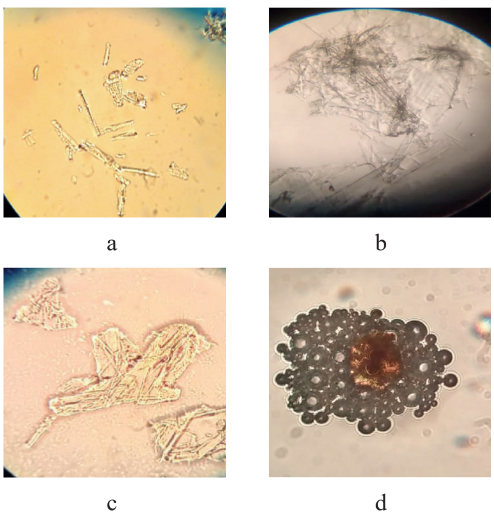


Figure 18 Foreign inclusions from the polymer stopper, 400× magnification: (a–c) polymer stopper surface, (d) cognac surface

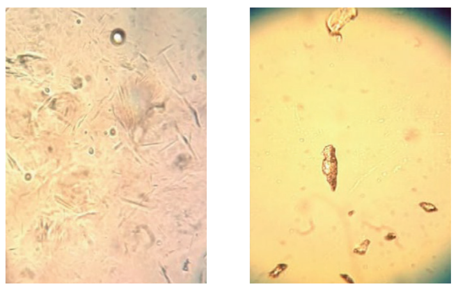


Figure 19 Microscope images of inclusions, 400× magnification

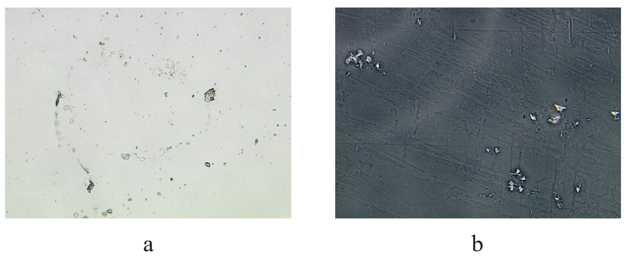


Figure 20 Microscope images of the stopper sample extract, 400× magnification: (a) model environment, (b) finished product

from the stopper surface into the model environments. Fig. 21 demonstrated inclusions similar in appearance and shape to those found in grape vodka. The particles were identical in structure, with minor differences in shape and size. Like in the cognac experiment, a sample of grape vodka was tested for phthalates to validate the assumptions about the nature of the inclusions.

The five samples of grape vodka came from the same batch and had the same bottling date. Their shelf-life was two months at the time of testing. Dibutyl phthalate was identified in all the samples at a concentration of 0.01–0.10 mg/L. Dioctyl phthalate was detected only in two samples at a concentration of 0.01 mg/L (Table 2).

The model environments contacted with T-shape polymer stoppers with different types of flanges: model environment 1 + wooden flange stopper (Fig. 21a); model environment 2 + T-shape stopper with wood-covered flange (Fig. 21b); model environment 3 + T-shape stopper with goldish metal-covered flange (Fig. 21c); and model environment 4 + T-shape stopper with blue metal-covered flange (Fig. 21d). The contact period was 10 days at 5–30°C, as stipulated in Technical Regulation of Customs Union 005/2011, Appendix 1 (Table 2).

Since beverages often become contaminated with microplastics during processing and packaging [35], the phthalates could be attributed to the production process. However, the second test, which took place six months later, showed an increase in the phthalate concentration (Table 2). The cognac sealed with sample 1 had 0.26 mg/L of dibutyl phthalate and 0.08 mg/L of dioctyl phthalate. Sample 2 demonstrated a lower migration rate: 0.20 mg/L of dibutyl phthalate and 0.05 mg/L of dioctyl phthalate.

The continuous migration of phthalates from the stopper would eventually render the cognac unsafe for human health. In addition, the EAEU standards for stoppers prohibit dibutyl phthalate migration. Appendix 2 of Technical Regulation of Customs Union 005/2011 limits the permissible amount of dioctyl phthalate migration as ≤ 2.0 mg/L per ten days of contact.

The grape vodka experiments also revealed a tendency for dibutyl phthalate and dioctyl phthalate to migrate during storage. However, their concentration was much lower than in the cognac: 0.01–0.11 and 0.09–0.18 mg/L after six months of storage (Table 2).

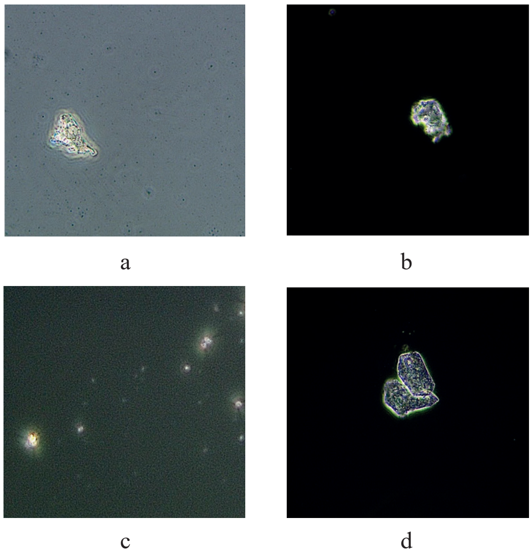


Figure 21 Microscope images of sediment separated from the model environment after contact with various capped polymer stoppers, 400× magnification: (a) wooden flange, (b) T-shape with wood-covered flange, (c) and (d) T-shape with metal-covered flange

Table 2 Stopper-to-beverage phthalate migration during storage at 5–30°C

Sample	Content, mean value, mg/L			
	Dibutyl phthalate		Dioctyl phthalate	
	Initial	After 6 months	Initial	After 6 months
Cognac, sample 1	0.180 ± 0.034	0.260 ± 0.049	0.010 ± 0.002	0.080 ± 0.013
Cognac, sample 2	0.170 ± 0.032	0.200 ± 0.038	0.003 ± 0.005	0.050 ± 0.002
Grape vodka, sample 1	0.010 ± 0.002	0.080 ± 0.015	0.050 ± 0.008	0.110 ± 0.018
Grape vodka, sample 2	0.010 ± 0.002	0.110 ± 0.021	0.010 ± 0.002	0.090 ± 0.014
Grape vodka, sample 3	≤ 0.001*	≤ 0.001*	0.100 ± 0.016	0.180 ± 0.029
Grape vodka, sample 4	≤ 0.001*	0.030 ± 0.006	0.030 ± 0.005	0.130 ± 0.021
Grape vodka, sample 5	≤ 0.001*	0.010 ± 0.002	0.010 ± 0.002	0.100 ± 0.016
Model environment 1 (40% water-alcohol solution + wooden flange stopper, Fig. 4a)	≤ 0.001*	≤ 0.001*	≤ 0.001*	≤ 0.001*
Model environment 2 (40% water-alcohol solution + T-shape stopper with wood-covered flange, Fig. 4b)	≤ 0.001*	0.010 ± 0.002	0.010 ± 0.002	0.010 ± 0.002
Model environment 3 (40% water-alcohol solution + T-shape stopper with goldish metal-covered flange, Fig. 4c)	≤ 0.001*	0.010 ± 0.002	0.010 ± 0.002	0.010 ± 0.002
Model environment 4 (40% water-alcohol solution + T-shape stopper with blue metal-covered flange, Fig. 4d)	≤ 0.001*	≤ 0.001*	≤ 0.001*	≤ 0.001*

* – the result is below the detection range

Figure 22 Contamination on the surface of T-shape polymer stoppers

No dibutyl phthalate was originally detected in grape vodka samples 4 and 5; after six months of storage, it remained as low as 0.01 mg/L. The model environments demonstrated similar results. Model environments 1 and 3 developed dibutyl phthalate overtime, but model environments 2 and 4 remained free of toxic compounds the entire storage time.

To sum it up, the domestic wine market has polymer stoppers that meet safety requirements in terms of phthalate migration alongside with similar stoppers that fail to comply with this control criterion. Obviously, the incoming control should be stricter for wineries that use this type of stoppers.

The appearance of stoppers is another urgent issue. The visual inspection of capped stoppers detected foreign particles, e.g., lint, dust, black stripes, etc. (Fig. 22). According to State Standards 32626-2014 and 34257-2017, polymer stoppers are stored in boxes or bags that protect their quality from contamination, precipitation, and mechanical damage. However, these regulatory documents establish no requirements for the sanitary conditions of the stopper surface. Moreover, they provide no instructions, even of a recommendatory nature, for the pre-bottling treatment. The drinks, on the contrary, are subject to serious quality and safety standards.

Naturally, the absence of sanitary standard and/or recommendations for preliminary processing renders stopper manufacturers unaccountable, while beverage producers have no legal grounds for appropriate demands and claims.

Stoppers with contaminated surface obviously affect the quality of the drink during storage and may lead to microbial spoilage.

CONCLUSION

This research assessed the safety and quality of polymer stoppers on the Russian market, as well as their impact on the finished products. Such aspects as appearance, shape, polymer dust, and sensory properties (changes in flavor, color, and transparency) met the standards introduced by State Standard 32626-2014. However, the low-cost cast stoppers and the medium-cost coextruded stoppers demonstrated permeability, which increased after hot-process bottling. All types of stoppers, except the medium-price coextruded samples, gave the aqueous extract a foreign smell.

The surface contamination detected in some samples is a strong reason for a stricter quality control. The expenditures on preliminary sanitation could be compensated by eliminating potential financial losses from the finished products rejected by inspectors.

In this research, the polymer stoppers proved to contaminate alcoholic beverages with toxic and potentially hazardous substances, such as ethyl acetate, heptane, hexane, acetone, dibutyl and dioctyl phthalates, as well as propyl, butyl, isobutyl, and methyl alcohols. All these substances accumulated during storage as a result of continuous migration from the faulty stoppers.

Based on the research results, beverages with ≥ 30% of alcohol sealed with polymer stoppers should be stored at ≤ 20°C.

Wine-making enterprises should be more careful in planning their production of it involves polymer stoppers because the stopper-beverage migration rate of toxic substances, such as phthalates, is the fastest during the first 7–10 h.

Although this research focused on the polymer stoppers available on the Russian market of alcoholic beverages, the results obtained could be relevant for winemakers from other countries, especially in the Eurasian Economic Union.

CONTRIBUTION

L.E. Chemisova and N.M. Ageyeva developed the research concept and design and wrote the manuscript. L.E. Chemisova, N.M. Ageyeva, O.N. Sheludko, and Yu.F. Yakuba provided data collection, analyzed the material, and proofread the manuscript. M.V. Antonenko systematized the experimental data. All the authors approved of the final version of the manuscript and are equally responsible for the integrity of the article.

CONFLICT OF INTEREST

The authors declared no conflict of interests regarding the publication of this article.

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