RESEARCHES ON THE STABILITY AND SHELF-LIFE OF CANNED TOMATOES

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Abstract: *There is a series of internal and external factors in the food chain that influence the shelf-life of the packaging system- food stuff: the selection and quality of the raw materials, the fabrication network, the processing and conservation techniques, the packaging, storage and distribution for the consumers. The analyze of the long term stability of the lacquer layer in the case of the tin canned tomatoes with different lacquers (3 systems of epoxy phenolic lacquer) was accomplished to compare the protection abilities of the lacquers and the extension of the shelf-life. The analyze was done initially and along the storage and focused upon: the characteristics of the inner lacquer layer; the sensorial and physico-chemical characteristics of the product as well as the metal content (AAS). The results obtained were the following: the porosity of the lacquer layer on the empty cans as well as on the tested cans during the storage of 1 and respectively 2 years did not suffer any modifications. During the two analyzed periods of storage the sensorial properties and the physico-chemical ones of the product „Tomatoes paste", including the heavy metals, differ according to the protection lacquer type of the cans: for the cans with white lacquer there are no modifications while for the cans with yellow lacquer, for both situations after 2 years of storage there are significant sensorial modifications due to the aggressiveness of the product content.*

Keywords: *cans, lacquer layer, storage, inner layer, outer layer*

1. Introduction

A very common material for food packaging is steel, in the form of metallic containers (cans). The steel cans are generally obtained by mechanical deformation from tin plated steel sheets and coated with an organic lacquer in order to increase the corrosion protection. [1]

The corrosion degradation of the packaging must be carefully controlled, not only because the packaging integrity must be preserved, but also in order to avoid any significant contamination of the food or drink, compromising the flavour. [1,2]

At a high temperature (sterilization) the resins that are part of the protection lacquers can decompose into components with toxic potential and can migrate from the package into the food stuff.[3,4]

Testing migration from food contact materials (FCM) in just four liquid simulants covering the whole range of foods is an ingenious concept, as it greatly simplifies compliance testing.[5]

According to the UE Directive 82/711EEC, the four simulants are: simulant A- water for the liquid foods, with a pH higher than 4.5; simulant B -3% acetic acid in water for the acidic liquid foods with a pH lower than 4.5; simulant C -10% aqueousethanol for the alcoholic products and simulantul D – olive oil for the fat foods[6].

The protection degree of the lacquers applied on the inner and outer surface of a can is a fundamental property for its commercial life that is determined according to the physico-chemical traits of the polymer, its application conditions, its compatibility with the food stuff and the metal support [7,8].

In order to increase the coating performance and the food compatibility, new organic coatings are under development with very high protective properties, with the final aim to increase the shelf life of the product.[9,10]

Both chemical and physical characteristics of the coating and metal substrate may influence the adhesion properties of the organic paint. It is well known that the higher adhesion is possible when the coating reacts (chemically and/or mechanically) with surface of metal. [11]

2. Experimental

The characteristics of the lacquer layer were analyzed after oven thermostating at 50°C, for a month (30 days) and respectively 2 months (60 days) in shelf storage conditions after 12 months.

The analyzing of the inner appearance of the lacquer layer of a representative set of opened cans was done piece by piece and it was compared with the conditions from the product standards. The porosity of the lacquer layer was also analyzed piece by piece for the entire set of opened cans (the average values being presented in the following tables).

For the ensemble metallic material-lacquering system the following tests were done:

1. The drying time

2. The determination of the weight of the dry lacquer layer is done by the gravimetric method: the vial of 10 x 5 cm is weighted then introduced in a solution mixture of 8% NaCl and 12% şi butyl glycol and after the lacquer layer removal the vial is weighted again. By difference and reporting to m^2 the dry film is determined [g/m^2].

3. The lacquering appearance

4. The adhesion before and after the sterilization is realized with the aid of a Tessor adhesive band with a surface of 1 cm (1 x 1 mm), figure 4.2.

5. The porosity of the lacquer applied on the can and the possible scratches on the body or on the bottom of the can were tested with the aid of a porosimeter Sencon SI 9000 plus, formed by two parts: 1) a special device ; 2) the measurement device.

The test consist in measuring a continuous electric flow established between the metal of the can and an electrolyte contained by the can as the effect of a constant potential difference existing between the can and an electrode placed in the electrolyte. The intensity of the flow is directly proportional with the lacquer porous areas and the possible scratches. The electrolyte must be at a room temperature of 17-23 °C.

The lacquer quantity applied and the lacquer technology was established by the metallic packages manufacturer according to the technical specifications of the lacquers and tins used. The lacquer layer porosity was determined both on the empty cans and also on the cans tested in the presented storage conditions. The analysis was done with the porosimeter according to a control method of the welded can.

The results regarding the bisphenol A content (BPA) obtained by the gas chromatography coupled with the mass spectroscopy (GC-MS) method are presented in Table 5. The GC-MS method allows the accurate identification and dosage of bisphenol A (BPA), according to the mass fragment 213, characteristic for that. On the basis of the measured areas from the spectrograms can be calculated with a great accuracy the BPA concentrations. The values determined by this method are strictly individualized for BPA.

Due to all this things the GC-MS method is the most indicated for the dosage of bisphenol A content.

3. Results and Discussion

The initial characteristics of the lacquer layer were tested according to the analyzing standards and presented values corresponding to: the layer sterilization resistance in the B, C, D and E solutions (STAS 1687/1-1981); the adhesion of the lacquer layer before and after the sterilization (SR ISO 2409:1995); the lacquer quantity applied (weight/m^2).

Table 1.

The initial characteristics of the lacquer layer – *vegetable products cans*

Characteristics	Tomatoes paste/ white lacquer	Tomatoes paste/ yellow lacquer 1	Tomatoes paste/ yellow lacquer 2
The layer sterilization resistance: - solution B - solution C - solution D - solution E	Lacquer layer appearance: -appropriate - appropriate -appropriate - appropriate	Lacquer layer appearance: -appropriate - appropriate -appropriate - appropriate	Lacquer layer appearance: -appropriate - appropriate -appropriate - appropriate
Weight/m^2 (dry lacquer)	8.2 – 8.36	10.76 – 12. 04	15.76 – 16.08
Layer adhesion: -before sterilization -after sterilization	- good - good	- good - good	- good - good

Table 2.

The inner appearance of the can – *vegetable products cans*

Characteristics	Storage conditions			
	Initially	After 1 month at 50^0C	12 months of shelf storage	24 months
Inner appearance of the can (lacquer layer): **- Tomatoes paste/ White lacquer**	The lid and metal can don't present black spots or rust, exfoliations or wrinkles of the lacquer layer.	The lid and metal can don't present black spots or rust, exfoliations or wrinkles of the lacquer layer.	The lid and metal can don't present black spots or rust, exfoliations or wrinkles of the lacquer layer.	The lid and metal can don't present black spots or rust, exfoliations or wrinkles of the lacquer layer.
Inner appearance of the can (lacquer layer): **- Tomatoes paste/ Yellow lacquer** 1	The lid and metal can don't present black spots or rust, exfoliations or wrinkles of the lacquer layer.	The can- lacquer layer exfoliated in points on the wrinkles and areas with a surface 1- 2 cm^2, nearby the welding area	The can- lacquer layer exfoliated in frequent points on the wrinkles and areas with a surface 2-3 cm^2, nearby the welding area	The can- lacquer layer exfoliated in scarce points and areas with a surface of 1cm^2, nearby the welding area
Inner appearance of the can (lacquer layer): **- Tomatoes paste/ Yellow lacquer** 2	The lid and metal can don't present black spots or rust, exfoliations or wrinkles of the lacquer layer.	The can- lacquer layer exfoliated in points on the wrinkles and areas with a surface 0.5 cm^2, nearby the welding area	The can- lacquer layer exfoliated in frequent points on the wrinkles and areas with a surface 2-3 cm^2, nearby the welding area	The can- lacquer layer exfoliated in scarce points and areas with a surface of 1cm^2, nearby the welding area

The analysis of the Tomatoes paste cans after the oven thermostating at 50°C indicated a degradation of the layer in the case of the yellow lacquer applied in one or two layers. The degradation was more intense after two months in comparison with one month of thermostating. The analysis of the cans after one year of shelf storage presents exfoliations in different points and areas situated nearby the welding area these being more intense for the cans with one layer of yellow lacquer. In both lacquering cases with this type of lacquer after one year of shelf storage the layer degradations are less intense than those seen after one month of thermostating.

Table 3.
The verifying of the lacquer layer porosity – *vegetable products cans*

Characteristics	Storage conditions			
	Initially	After 1 month at 50^0C	12 months of shelf storage	24 months
Layer porosity. mA: **- Tomatoes paste/ White lacquer**	43.3	43.5	44.5	42.8
Layer porosity. mA: **- Tomatoes paste/ Yellow lacquer** 1	71.9	72.2	73.5	72.8
Layer porosity. mA: **- Tomatoes paste/ Yellow lacquer** 2	51.9	52.8	57.9	53.0

The results subscribed to the following technological standards:
- max. 112 mA – vegetable cans;
- max. 89 mA – meat in natural juice cans.

After the oven thermostating at 50°C: for one month and respectively for two months the characteristics of the white lacquer layer and that of the yellow lacquer layer for the product Tomatoes paste do not suffer significant modifications. The same thing is available after one year of shelf storage.

Table 4.
The verifying of the lacquer layer porosity – *vegetable products cans*

No.	Name / source	Chemical nature	Extraction environment	Extraction conditions/ Extraction ratio	Global migration, [ppm]	Metals release, [ppm]	
						Pb	Cd
0	**1**	2	3	4	7	8	9
1	**GOLD HE 1526-13** 1 layer ICI Packaging Coatings	Epoxyphenolic	distilled water	1h, 121°C/ 1:1	7.75	-	-
			3 % acetic acid sol	1h, 121°C/ 1:1	9.75	0.012	0.000
			isooctane	48h, t.c./ 1:1	4.75	-	-
2	**GOLD HE 1526-13** 2 layers ICI Packaging Coatings	Epoxyphenolic	distilled water	1h, 121°C/ 1:1	9.0	-	-
			3 % acetic acid sol	1h, 121°C/ 1:1	11.5	0.019	0.000
			isooctane	48h, t.c./ 1:1	5.5	-	-

3	**PL 1333-16** GRACE DAREX GmbH	Epoxyphenolic	distilled water	1h, 121°C/ 1:1	9.5	-	-
			3 % acetic acid sol	1h, 121°C/ 1:1	16.5	0.015	<0.006
			isooctane	48h, t.c./ 1:1	7.0	-	-
4	**VITALURE 344 Cod 16-4344 L** ICI Packaging Coatings	Epoxyphenolic	distilled water	1h, 121°C/ 1:1	11.5	-	-
			3 % acetic acid sol	1h, 121°C/ 1:1	24.0	0.014	0.000
			isooctane	48h, t.c./ 1:1	5.25	-	-
5	**VITALURE 334 Cod N 49234** ICI Packaging Coatings	Epoxyphenolic	distilled water	1h, 121°C/ 1:1	19.0	-	-
			3 % acetic acid sol	1h, 121°C/ 1:1	26.75	0.048	<0.001
			isooctane	48h, t.c./ 1:1	9.0	-	-
6	**GZ 036 SPT** POLONIA	Epoxyphenolic	distilled water	1h, 121°C/ 1:1	10.5	-	-
			3 % acetic acid sol	1h, 121°C/ 1:1	18.25	0.007	0.001
			isooctane	48h, t.c./ 1:1	6.5	-	-
7	**Sulf resistent lacquer L 3312** POLICOLOR Romania	Epoxyphenolic	distilled water	1h, 121°C/ 1:1	21.0	-	-
			3 % acetic acid sol	1h, 121°C/ 1:1	29.75	0.024	<0.006
			isooctane	48h, t.c./ 1:1	6.5	-	-
8	**Acid resistant lacquer L 3311** POLICOLOR Romania	Epoxyphenolic	distilled water	1h, 121°C/ 1:1	16.5	-	-
			3 % acetic acid sol	1h, 121°C/ 1:1	18.25	0.029	<0.006
			isooctane	48h, t.c./ 1:1	-	-	-

Table 5.

The bisphenol content in the protection lacquers for the food cans

No.	Name / source	Chemical nature	Extraction environment	Extraction conditions/ Extraction ratio	Bisphenol content, [ppm]
					GC - MS
1	**HE 1526-13** Gold 1 layer ICI Packaging Coatings	Epoxyphenolic	distilled water	1h, 121°C/ 1:1	-
2	**HE 1526-13** Gold 2 layers ICI Packaging Coatings	Epoxyphenolic	distilled water	1h, 121°C/ 1:1	1.08
3	**PL 1333-16** GRACE DAREX GmbH	Epoxyphenolic	distilled water	1h, 121°C/ 1:1	0.3
4	**PL 1014-69** Gold GRACE DAREX GmbH	Epoxy-modified	distilled water	1h, 121°C/ 1:1	0.85

5	**VITALURE 344 Cod 16-4344 L** ICI Packaging Coatings	Epoxyphenolic	distilled water	1h, 121^{o}C/ 1:1	> 3.0
6	**VITALURE 334 Cod N 49234** ICI Packaging Coatings	Epoxyphenolic	distilled water	1h, 121^{o}C/ 1:1	0.15
7	**GZ 036 SPT** POLONIA	Epoxyphenolic	distilled water	1h, 121^{o}C/ 1:1	0.19
8	**Sulf resistent lacquer L 3312** POLICOLOR Romania	Epoxyphenolic	distilled water	1h, 121^{o}C/ 1:1	0.02

The values obtained for the BPA presented in Table 5 are the following:
- below the value of 1 ppm, for the chromatographic method GC-MS, for all the epoxyphenolic analyzed lacquers with the exception of the two layered HE 1526-13, lacquer;
- extremely high values obtained for the Vilature 344 lacquer, for both methods not recommended for the hygienic - sanitary approval.

4. Conclusion

On the basis of the studies presented we can conclude the fllowings:
- the values obtained for the global migration of the components in all the extraction environments are situated below the admitted value of 60 ppm;
- the heavy metals release are below the admitted values : the Pb are way below 0,1 ppm, and the Cd is situated below the detection value of the device of 0,006 ppm;
- the UV fluorescence indicated the absence of the condensed polynuclear aromatic hydrocarbons;
- there was no detection of the following components: epichlorohydrin in the epoxyphenolic lacquers, acetaldehyde in the modified polyester lacquer and amines in the modified epoxy aminic lacquer.

5. References

[1]. F. DEFLORIAN., S. ROSSI., M. d. C. VADILLO., M. FEDEL., Electrochemical characterisation of protective organic coatings for food packaging, J Appl Electrochem, 39:2151–2157, DOI 10.1007/s10800-009-9818-1, (2009)
[2]. Bernardo PEM, dos Santos JLC, Costa NG (2005) Prog Org Coat 54:34
[3]. Marcus P, Mansfeld F (eds) (2006) Analytical methods in corrosion science and engineering. Taylor and Francis, London
[4]. Begley, T. (2006). From Migration to Exposure: FDA experience. Lecture held at the closing conference of the EU project Foodmigrosure. Baveno, Italy, September 27/28, 2006.
[5]. Koni GROB., The future of simulants in compliance testing regarding the migration from food contact materials into food, Food Control 19, 263–268, (2008)
[6]. Barilli F, Fragni R, Gelati S, Montanari A (2003) Prog Org Coat
[7]. B. RAMEZANZADEH., M.M. ATTAR., An evaluation of the corrosion resistance and adhesion properties of an epoxy-nanocomposite on a hot-dip galvanized steel (HDG) treated by different kinds of conversion coatings, Surface & Coatings Technology, doi: 10.1016/j.surfcoat.2011.04.001, (2011)
[8]. Robertson GL (2006) Food packaging: principles and practice. CRC Press/Taylor and Francis, London
[9]. Bonora PL, Deflorian F, Fedrizzi L (1996) Electrochim Acta 41:1073
[10]. Mojica J, Garcia E, Rodriguez FJ, Genesca´ J (2001) Prog Org Coat 42:218
[11]. Rohwerder M, Turcu F (2007) Electrochim Acta 53:290