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Migration from the Internal Coatings of Food Cans and the Lids of Glass Jars: Campaign 2000 on the Swiss Market

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Introduction

During January to March 2000, 101 critical samples of canned foods were collected in the region of Zürich, which can be considered representative for the Swiss market. This campaign served for control, but also to provide a picture of the cans presently sold in Switzerland. In the last few years, the internal coatings of food cans have undergone fast changes. To contrast them with the past, published data on previous campaigns is summarized, all of which refers to cans produced in early 1998 or before.

Previous campaigns in Switzerland

In the early 1996, high concentrations of bisphenol A diglycidyl ether (BADGE) were found in many canned oily foods, primarily sea food in oil or sauces. Referring to the oil phase, 10 of 142 samples contained BADGE in excess of 10 mg/kg, another 22 between 1 and 10 mg/kg (1). Recalculated for the whole can content, BADGE concentrations exceeded 10 mg/kg in two samples and ranged between 1 and 10 mg/kg in 21 products (15%). The first part of this campaign took place before legal measures were taken (confiscation), while in the second, the worst cans had already been withdrawn from the shelves. As nearly all these products were imported, it is assumed that the results were representative for the European market at that time.

In the winter 1996/1997, the situation had improved drastically as a result of strict control by the Swiss trade: among 242 samples of oily or fatty products, a single one contained more than 1 mg/kg of BADGE (1.7 mg/kg plus 0.37 mg/kg of the

chlorohydrin BADGE.HCl) (2). Three samples contained more than 1 mg/kg of bisphenol F diglycidyl ether (BFDGE) and its monochlorohydrin (BFDGE.HCl). When 3- and 4-ring novolac glycidyl ether (NOGE) was included, seven samples exceeded 1 mg/kg, reaching up to 3.3 mg/kg. In July 1997, none of 30 samples selected as most critical contained more than 35 µg/kg of BADGE. One of them contained 110 µg/kg of BFDGE. However, screening by the importers and distributors through BFDGE missed detecting that six of these samples contained more than 1 mg/kg of 3- to 5-ring components of novolac glycidyl ether (NOGE), with a maximum of 14.4 mg/kg in a canned tuna (about 20 mg/kg with the 6-ring NOGE and the chlorohydrins). The BFDGE content was extremely low (7 µg/kg in the sample with the maximum concentration of NOGE), which indicates that NOGE cannot be reliably detected using BFDGE as an indicator.

In summer 1998, 270 samples of canned aqueous foods were analyzed (3). No BADGE or NOGE with epoxy functions were found and, hence, the survey focused on the chlorohydrins. 11 samples (4%) exceeded legal restrictions. Four contained more than 1 mg/kg of BADGE chlorohydrins (maximum of 8.6 mg/kg), while the other seven contained NOGE. BFDGE chlorohydrins were determined at concentrations between 0.34 and 2.9 mg/kg. Nine of the 11 contested samples concerned sweet corn and asparagus.

Previous campaigns in other countries

Summerfield et al. (4) analyzed samples bought between 1995 and 1997 from the British market. BADGE concentrations exceeded 1 mg/kg in seven of 15 samples of anchovies in oil (4 of which even exceeded 10 mg/kg) and five from 22 samples of sardines in oil. All of the 20 samples of tuna contained less than 20 µg/kg of BADGE, but were probably more than two years old. Considering that BADGE concentrations decrease by a factor 10–20 per year, this is little indicative about the BADGE content at the time most of these products were consumed.

In 1997–1999, *Uematsu et al.* analyzed cans from the Japanese market. In a first survey (5), BADGE (without the chlorohydrins) was found in 11 from 16 samples of canned fish. In four products, its concentration exceeded 1 mg/kg and reached 12.9 mg/kg in a tuna in oil. In 1998 (6), 26 products were analyzed. BADGE concentrations were always below 1 mg/kg, but the sum of BADGE, its dimer and trimer reached 15 mg/kg. Four samples contained NOGE, with a maximum for the sum of the 2- and 3-ring components of 6.9 mg/kg.

Simoneau et al. (7) reported results on BADGE from 382 samples of canned fish in oil from all EU member states and Switzerland, bought in 1997, and estimated the exposure to be below 9 μ g per person and day. In merely 3% of the products, mostly anchovies, BADGE exceeded 1 mg/kg (8) and reached up to 11.8 mg/kg. This was a substantial improvement compared to the Swiss and the British results from 1996. In 1999, *Theobald et al.* (9) published data showing that no sample of canned milk products contained BADGE in excess of 1 mg/kg. *Rauter et al.* (10) determined BADGE and its hydrolysis products in 67 samples from the Austrian market. 16% of these exceeded the 1 mg/kg limit (without including the chlorohydrins). The date of sample collection was not indicated, but could have been winter 1997/1998.

Legal restrictions on BADGE and NOGE

According to EU toxicological assessments and legislation, the sum of BADGE, its monohydrolysis product (BADGE.H2O), and its chlorohydrins (BADGE.HCl, BADGE.2HCl, and BADGE.H2O.HCl) should not exceed 1 mg/kg in the can content. In Switzerland, there is an additional limit for BADGE of "not detectable at a limit of 20 µg/kg". The use of NOGE has not been authorized in any European country and is considered illegal in Switzerland. In a letter to the EU authorities dated 8 February 2000, the Joint Industry Group (JIG), representing the producers of resins, additives, lacquers, coated cans, and canned foods, made the commitment to phase out the use of NOGE as additive to organosol coatings in Europe. In the EU, the use of NOGE as additive will probably be banned. These restrictions largely determined the tasks of our analyses.

Analytical strategy

The analysis was focussed on critical samples by taking into account results from previous investigations (1,4).

- 1. In foods without a coherent fat or oil phase, coating-related epoxy compounds are hydrolyzed and only chlorohydrins are of concern.
- 2. Relevant migration of NOGE is only expected from organosol (PVC) coatings (including side stripes).
- 3. BADGE- or NOGE-related chlorohydrins in concentrations exceeding 200 µg/kg are only found in cans with organosol coatings. Thus, among the cans with aqueous foods, only those with organosols need to be controlled.

Derived from this experience, the following analytical strategy was applied (fig. 1).

- 1. Cans containing aqueous foods were emptied and the coatings of all parts checked on the presence of organically bonded chlorine, applying the Beilstein test.
- 2. Aqueous foods in Beilstein-negative cans (epoxy or polyester coatings) were not further analyzed, since the concentrations of the chlorohydrins in the foodstuff can be assumed to be below 200 µg/kg and epoxy compounds hydrolyzed. In a few selected samples (white epoxy/anhydride lacquers), BADGE.2H2O was determined.
- 3. Cans with Beilstein-positive coatings were extracted with acetonitrile. If BADGE, NOGE, or related chlorohydrins were detected in the lacquer, the can content was homogenized and analyzed for chlorohydrins. Otherwise the analysis was stopped.

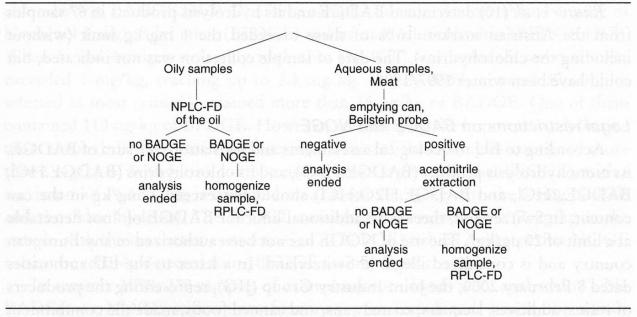


Figure 1 Scheme of the analytical procedure

4. For oily foods, the oil was analyzed by normal phase HPLC (NPLC) in order to determine BADGE, NOGE and reaction products thereof, including reaction products of BADGE with phenols (chain stoppers) and hydroxylic solvents. In case of positive findings, the can content was homogenized, extracted, and analyzed.

Analyses were performed by reversed phase HPLC (RPLC) and fluorescence detection (FD), NPLC-FD, or GC-MS, sometimes involving size exclusion chromatography (SEC) for fractionating food extracts. These methods were described in the literature (11–13).

Samples

The selection of the products to be analyzed focussed on the can types and foods considered most critical based on the results of previous campaigns. Hence, only few cans with fruits, tomatoes or vegetables in aqueous media were analyzed, but many with sweet corn and asparagus. Oily or fatty foods (such as fish in oil, meat, soups, or sauces), cans with easy open end, and 2-piece cans were selected preferentially. Since about half of all the canned products sold in Switzerland are tomatoes, vegetables, and fruits, and also numerous other products were disregarded, at best a third of the assortment was sampled (table 1).

Table 1 Samples analyzed within the	campaign	
Total of cans analyzed	101	he Caner built be been pointed to an
products in water	72	
products in oil	29	
Products in glass jars	5	

Samples were from all major food distributors in the Canton of Zurich except small speciality shops. Products imported in small numbers, often from exotic countries, were not included into the survey. Samples were taken in a number approximately corresponding to the importance of the distributor.

Results

Results are summarized in table 2. The second column characterizes the cans by the number of pieces (3-piece cans consisting of a side wall and two ends, 2-piece cans of a deep-drawn cup and a lid) and the color of the internal coating. The three columns under the heading of "Beilstein test" indicate the presence or absence of organically bonded chlorine in the coatings of the cup or side wall, the lid (and bottom end for 3-piece cans), and the side stripe (welded side walls). The concentrations in the can contents listed under summed BADGE refer to the components included in the 1 mg/kg EU-limit. BADGE.2H2O is listed separately. The column "NOGE <1000 D" lists summed concentrations of NOGE epoxy and chlorohydrin components up to 1000 D (including 6-ring compounds). Under "can extracts by acetonitrile", concentrations referring to the total can volume are reported. When RPLC-FD or NPLC-FD did not show a significant peak, the chromatogram is characterized by "empty". The glass jars nr. 107–110 were collected in summer 1999, and the values given under NOGE merely refer to the 2-ring components.

Side stripes

69 of the 101 cans consisted of 3-pieces with welded bodies and usually a side stripe on the seam. 16 side stripes were Beilstein-positive, seven of them contained BADGE, 2 NOGE, and seven contained neither BADGE nor NOGE.

Calculated on the can volume, acetonitrile extracted 250 and 400 μ g/l of NOGE and its chlorohydrins (MW <1000 Dalton) from cans nrs. 14 and 71. No NOGE was detectable in the foods at a detection limit of 50 μ g/kg. The seven BADGE-containing side stripes released between 125 and 10,000 μ g/l of the epoxy compounds and chlorohydrins into acetonitrile and up to 410 μ g/kg of hydrolyzed chlorohydrins into the food (sweet corn, sample nr. 82).

Apparently side stripes may contain widely varying amounts of BADGE and NOGE. Migration of the chlorohydrins into aqueous foods did not reach 1 mg/kg. However, it would exceeded 1 mg/kg for the chlorohydrins plus the epoxides if these cans had been filled by an oily food. Assuming that 50% of BADGE or NOGE are extracted into the food (extreme values are beyond 80%), migration would have exceeded 1 mg/kg in 2 out of 7 cans analyzed.

Two-piece cans

32 samples consisted of deep-drawn 2-piece cans. Merely eight of them had a Beilstein-positive coating in the cup. Six of these eight samples released neither BADGE nor NOGE. On the other hand, both samples with BADGE in the

Table 2		8 8 8 468 8 5 8	2 2 2 2
Samples analyzed and results. Can type, 2- or	3-piece cans; ea, easy ope	en lid; g, gold lacquer; w	v, white; m, opaque.
Net, labelled net weight. Origin, country of or	gin		

	8-#- F									ligration (
Nr.	Can		Net	Origin	Product		ilstein		Cards and a second second	DGE	NOGE	Can extract
CL	cup	lid	(g)		PA # 23 21	Cup	Lid	Stripe	Sum	.2H2O	< 1000 D	acetonitrile
1	2 g	ea g	27	E	Anchovies in oil	+	-		< 5	40 11 ²	< 10	
2	2 g	ea g	50	E	Anchovies in oil	+	+		< 5	12.2.3	< 10	같이 그 등 안 같
3	2 g	ea g	50	E	Anchovies in oil	12	-		< 5	19 g. 6	< 10	
4	2 g	lea g		E	Anchovies in oil	+	-		< 5	1 ca 2 1	< 10	R. 19 8 817 8
5	3 m	g	390	E	Artichokes		-	부분함	S SAE	263	1 2 F K. 1 2	말 / ~ ~ 등 말 ㅋ
6	3 gm	gm	215	RSA	Asparagus	0-01		王王皇	音 山高田	864	55 Z. A.	1 - T - F
7	3 gr	gr	280	China	Asparagus		_	+	14 (j. 2. C	1 20 2 3	1 28 2 6 4	empty
8	3 gm	gm	290	RSA	Asparagus	1 - T	-1_	2 4 8	8 83 4	1 cm 2 6		
9	3 g	g	280	China	Asparagus	1 - 1	-42	+	916217		~ 꽃 영 앱	NOGE?
0	3 g	g	280	China	Asparagus	2 J - A		+	9 BH	8 8 6	2.12.13	empty
1	3 g	g	425	USA	Asparagus	8	-412	슬 끝 없.	G BE X		1. H	1 S. C. M.
2	3 g	g	400	D	Baby corn	1 - 1 - 1	<u></u>	2 2 8	8- 89 S	1 2 2 3	6 6 8	The 1944 A
3	3 g	g	230	Thailand	Bamboo shoots	- S	-	61 i - 181	584		The second	김 사람은 요즘 문.
4	3 g	g	400	F	Beans	0 9 - 11	-	+	8 7 8	14 島島	< 100	NOGE: 400 µg/l
5	3 w	w	425	CH	Beans	-	-	필 유 정	068	480	1.420 2.4	
6	3 gm	gm	420	E	Beans	-	-	일 걸 같.	6 8 A	13. 8. 1		目前の問題で
7	3 w	g	800	F	Beans		-	일 문 요.	8 5 1	5 20 3	. E. 7 22.	國 开始法
8	3 m	m	450	USA	Beans	2	-45	+	270	310		BADGE: 0.6 mg/l
9	3 w	w	550	D	Cabbage	-	<u>-</u> 6	영 수 값	学 臣 之	14688	- 22 - 4	
0	3 g	g	340	GB	Corned beef	-	<u> </u>	8 G 8/	百八日	8 38 3	- 61 3 8	
1	3 mg	mg	340	Brazil	Corned beef	1 2 - 3	-	한 음 생	3 17 -	1. 3. 3	- 97 g. 21	8
2	2 gm	lea gm	190	D	Fish in sauce	+	+		< 5	18 42	< 10	E 6 A 6 3
3	3 w	w	430	CH	Fruits	-	-	응 두 성	8 E 1	< 40	- 6 6 4.	2 × 2
4	3 w	ea w	310	CH	Meat			8-14-8	81.9	1 th 2 3		
5	3 w	w	195	CH	Meat loaf	-	-	을 끌 쉽	5 6 A	2.6.9		
6	3 w	ea g	140	I	Meat loaf	6-10		S. L. K.	5 0 d	2 5 3		a 5 2 5 6 6
7	2 g	g	120	CH	Meat loaf	-	+		<u>a</u> , 27 8	12.8 4	1000	NOGE: 5 mg/l

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									M	ligration ('µg/kg)	
Nr.	Car	type	Net	Origin	Product	I Be	ilstein	test	BA	DGE	NOGE	Can extract
	cup	lid	(g)	Thurland	Tuna in oil	Cup	Lid	Stripe	Sum	.2H2O	< 1000 D	acetonitrile
28	3 g	g	190	China	Mushrooms	_	_	+	255		22	empty
29	3 w	w	200	FL	Mushrooms	-		=	- 20		- 10	
30	3 m	m	400	PL	Mushrooms			-				
31	3 w	w	200	D	Mushrooms	-	-	Ŧ	5.5	540	20.1	monore un
32	3 g	g	184	China	Mushrooms	-	-	+	245	180	< 20	empty
33	3 g	g	184	PL	Mushrooms	-	-	-	and the second	210	<10 ×	B TO E I I I I I I I
34	3 w	w	200	PL	Mushrooms	-	-	-	199	310	10	BATY COLOR STATE
35	3 g	g	184	China	Mushrooms	-	-	π	280	250	20	BADCE 57 MAY
36	3 g	g	184	China	Mushrooms	-	-	+	204	920	10	empty
37	3 g	g	184	China	Mushrooms	-	_	Ξ.		130	N-	and reactions were bride
38	3 w	w	200	D E	Mushrooms	-	_	-		130		BADGE: 125 pl/l
39	2 m	ea m	140	E	Octopus in sauce	-	-		< 20	28	< 20	BADGE, 500 µM
40	2 g	ea g	115	GR	Octopus in sauce	+	- +		4200		< 5	and the second sec
41	2 g	ea g	160	GR	Octopus in sauce	+	+		< 5		< 10	NOCE
42	2 g	ea g	115	E	Octopus in sauce	+	+		< 5		< 10	MGGE manhair
43	3 g	lea g	180	GR	Octopus in water	-	-	-				NOCE SEATING
44	3 w	ea w	360	E	Olives	-	+	-	340		5122	BADGE: 1.2 mg/
45	3 w	w	425	CH	Peas	-	Ŧ	-	~ 30	470	248	
46	3 w	w	425	FL	Peas	-	-	-	65	320	42	NOCE
47	3 g	g	400	CH	Peas	-	-	-	16		20	NOGE
48	3 w	g	800	F	Peas	-	-	-	26		50	NOCH
49	2 w	g	400	F	Peas	-	+		1.1.1.5		25	empty
50	3 w	g	1000	F	Peas		a di serie <u>an</u> fai di serie	and a second	and a second second			
51	3 g	g	400	F	Peas	-	-	+				empty
52	3 w	w	850	CH	Ravioli	-	-	-				
53	3 w	w	240	CH	Salade	-	-	-	< 2	450	< 10	
54	3 g	g	80	D	Salmon	-	-	-				
55	2 w	ea w	125	E	Sardines in oil		-		< 5		< 10	
56	2 w	ea w	120	E	Sardines in oil	000	(4)		< 5	SH30-	< 10	acetoritrile
57	2 w	eaw	56	E	Sardines in oil	-80	078 <u>05</u> 370		84	39(1	MOGE	Can extract
58	2 w	ea w	125	Marocco	Sardines in oil	-	-		< 5	0.0300004	< 5	

PSI:	3.4.	1800 00	135	Maracca	Sardines in oil					ligration (µg/kg)	
Vr.	Can	type	Net	Origin	Product	Be	ilstein	test	BA	DGE	NOGE	Can extract
	cup	lid	(g)	Right, coa	द्राप्तपाल्च सः श्री	Cup	Lid	Stripe	Sum	.2H2O	< 1000 D	acetonitrile
59	2 m	ea g		Marocco	Sardines in oil	-	+		< 5	prestion 1	< 10	
50	2 g	lea g	States-	E	Sardines in oil	- 84	den a sin		< 5	050	< 10	Can average
51	3 g	g	283	CH	Sauce	-	171	Stand	Course	Sugar.	G enne m	anone white it is
2	3 gm	gm	290	Thailand	Sea food		en Pire Anter				n series de la serie La series de la serie	CHUDEA
3	3 gg	gg	400	D	Soup	-	-	_	14.3	1.1.1.1.1.1	<10	CAPACITA CONTRACT
4	3 w	lea w	380	D	Soup	1 <u>1</u>	-		1. 2.5.6		< 10	cushi)
5	3 w	lea w	420	FL	Soup	-		-	< 3 -		< 10	Perman V
6	3 w	lea w	400	D	Soup	<u> </u>		_	1. 634		<-10	
7	3 m	ea g	400	A	Soup	_		_				
8	3 w	eag	400	A	Soup		+	<u>_</u>		3.20		empty
9	3 g	eag	170	GR	Squids in sauce	_		<u></u>	< 20	120	< 20	lombei
0	3 g	ea g	440	Turkey	Stuffed peppers		- +	<u> </u>	< 10		5600	NOGE: 58 mg/l
1	3 g	and the second se	300	F	Sweet corn	State of the second		+			< 100	NOGE: 250 µl/l
2	2 w	g	340	F	Sweet corn	Ŧ	-		< S .		< 10	1400L. 250 µm
3		g	340	USA	Sweet corn	1 - 2		_	< 9		< 10	
'4	3 gm 2 w	gm	300	F	Sweet corn	-	- +	a (7 d)	1500		< 5	amatri
4 '5	2 W	g	340	USA	Sweet corn	144			< 30	75	< 20	empty BADGE: 500 µl/l
6	3 gm	gm	340	USA		-		+		130	and the second	BADGE: 125 µl/
	3 g	g	340	USA	Sweet corn	Contraction of the		+		150		DADGE: 125 µ1/1
7	3 g	g		USA	Sweet corn			7	200	250		DADOF 10 /
8	3 g	g	340		Sweet corn	-	Ξ.	+	380	250		BADGE: 10 mg/
9	2 g	g	340	USA	Sweet corn	+	Ξ.	7	3600	370		BADGE: 5.7 mg/
0	3 g	g	340	USA	Sweet corn			+	250	210		BADGE: 1.8 mg/
81	3 g	g	340	USA	Sweet corn		-	+	230	180		BADGE: 1.8 mg/
2	3 g	g	340	USA	Sweet corn			+	410	240		BADGE: 6 mg/l
3	3 m	ea g	400	I	Tomatoes	-						
4	3 w	W	400	I	Tomatoes	-			< 3. 1			
5	2 m	m	100	Thai	Tuna in oil	-			< 20	14.40	< 10	(cmbr)
6	2 gr	lea gm	92	Philippines			+		< 5		< 10	
37	2 m	m	100	Thailand	Tuna in oil	. CTD	D = D		< 5	121420	< 10	30910040499
8	2 m	m	200	Thailand	Tuna in oil	- 89	elis n eelo		< 5	DGE	< 20	Epoxy
9	2 m	m	200	Thailand	Tuna in oil	-	_		< 5	Bissboy -	< 5	NOGESSmelly

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N/		8	10/-4	1 Osisia				Beilstein test			(µg/kg)	New Sector
Vr.	cup	type lid	Net (g)	Origin	Product	Cup	Lid	test Stripe	Sum	DGE .2H2O	NOGE < 1000 D	Can extract acetonitrile
90	2 gm	g	170	F	Tuna in oil	1 (m 1) (m 1)	M <u>-</u> 8		< 5		< 5	主义并来 ?
91	3 g	ea g	160	I	Tuna in oil	8- 81.3	gg.	옷 을 것	19. OS 9	Sh y		요까뻐린린
92	2 m	m	185	Thailand	Tuna in oil	5 _8 -	8 -		图 医 第	1 E 1	18 是书	P & X & 2
93	一些 胃	10	185	Thailand	Tuna in oil	T - 3	6 -25	음식 코	< 5		< 20	855 S & S.
94	3 w	ea g	120	E	Tuna in oil	10 -44	\$ -S	표. 음 상	< 5	1 G 4	< 20	医骨骨骨炎 法
95	2 g	ea g	160	P	Tuna in oil		+		< 5		< 10	22 8 2 3
96	2 w	ea w	115	E	Tuna in oil	0 8 <u>-</u> 81	10 - 11 - 11 - 11 - 11 - 11 - 11 - 11 -	医产品	< 20	1	10	日前日名に
97	2 m	ea m	200	Thailand	Tuna in oil		8A.		< 5	1 2 1	20	한 번 및 등 두
98	2 m	m	100	Thailand	Tuna in oil	-	a -6		< 5	1 2 2	10	D. S. M. S. M.
99	3 w	ea g	160	I	Tuna in water	_	8-1-	許量 문	10 A. C	a second as	1 6 5	68454
100	2 m	m	200	Thailand	Tuna in water	b _ 2	8 -		100 B. C.		1. 2. 2. 2	教育 世界 的
101	3 g	ea g	280	GR	Vegetables in oil	-	1 N.	성운 실	≤ 150		< 20	
102	Glass j	ar	340	I	Dried tomatoes		+		的星之		< 50	NOGE
103	Glass j	ar	280	I	Artichokes	1 3. 35	+		684	1. 1	< 50	NOGE
104	Glass j	ar	280	I	Peppers		+		Con Street Co	1.1	220	NOGE
105	Glass j	ar	190	I	Pesto		+		100 B		< 100	NOGE
106	Glass j		280	I	Dried tomatoes	and the	+			1.5.1.5.1	< 50	NOGE
107	Glass j	ar*	5	I	Artichokes	a an ar	+		65		42	NOGE
108	Glass j	ar*	6 6 3	I	Artichokes		+		10		20	NOGE
109	Glass j		8 8 4	I	Dried tomatoes	1 5- 5	+		20	1	30	NOGE
110	Glass j		E Bri	I	Mushrooms		+		5	1.1	75	NOGE

organosol contaminated the content with BADGE and its reaction products at a level exceeding 1 mg/kg, confirming that BADGE- and NOGE-stabilized organosol coatings are still a high risk.

Sample nr. 40 in table 2 contained octopus in an oily tomato sauce, and the migration reached 2.4 mg/kg for BADGE, 0.4 mg/kg for BADGE.HCl, and 1.4 mg/kg for BADGE.2HCl. Also the lid was coated with a BADGE-stabilized organosol. Sample nr. 79 contained sweet corn; 1 mg/kg of BADGE.HCl.H2O and 2.6 mg/kg of BADGE.2HCl were detected. From the emptied can, acetonitrile extracted another 5.7 mg/l of non-hydrolyzed stabilizer, indicating that a third of the BADGE components were extracted by the aqueous food (from organosols, acetonitrile extraction is quite complete).

Easy open lids

35 cans carried an easy open lid, only 14 of which had a Beilstein-positive coating. In 10 of the PVC-containing lacquers, neither BADGE nor NOGE was detected. Of the four samples with BADGE- or NOGE-stabilized organosols, two clearly exceeded the 1 mg/kg limit and a third was at the limit.

Sample 27 contained meat loaf (meat cheese). The product was contaminated with about 1 mg/kg of largely hydrolyzed NOGE derivatives (insufficiently coherent fat phase). Acetonitrile extracted an amount of NOGE and its chlorohydrins from the lid corresponding to another 5 mg/l referring to the can content, reflecting relatively weak extraction by the food, perhaps owing to limited contact with the fat phase.

Sample nr. 70 consisted of stuffed peppers with some 15% of edible oil and was contaminated by 5.6 mg/kg of NOGE and its chlorohydrins. Acetonitrile extracted another 5.8 mg/l of these components, i.e. the food extracted about half of the NOGE originally present in the coating.

Results regarding migration

From the analytical results listed in Table 2, the following conclusions can be drawn regarding the canned foods.

- Four products violated Swiss regulations: stuffed peppers, sweet corn, meat loaf and octopus (see above). Three products contained more than 1 mg/kg of BADGE, NOGE, and their chlorohydrins, the forth about 1 mg/kg of NOGE. All four were products sold in rather small quantities, three of them through minor food distributors.
- 2. Two additional products contained NOGE in the side stripe, but no NOGE components were detected in the foods.
- 3. There was no further product exceeding the Swiss 20 µg/kg limit specifically for BADGE.
- 4. No product contained the restricted BADGE components at a concentration between 500 and 1000 µg/kg, and only six of those analyzed in the range between

100 and 500 µg/kg. For the products not further analyzed after a negative screening result, it can be assumed that concentrations were below 200 µg/kg.

- 5. The concentrations of BADGE.2H2O in aqueous foods packed in the frequently used 3-piece cans with a white epoxy-anhydride coating ranged between 200 and 500 µg/kg and did not significantly decrease since 1998 (4). Only a small proportion originated from BADGE or its hydrolysis products in the coating. Most BADGE.2H2O is the hydrolysis product of a still unknown material.
- 6. None of the oily products contained more than 100 μg/kg of BADGE monoreaction products, i.e. derivatives with one epoxy group and the other being reacted with a phenol or a solvent (14). However, there were rather few oily products in cans with epoxy coatings.

Products in glass jars

The internal coatings of twist-off caps for glass jars usually consist of organosols stabilized with NOGE. Previous investigations indicated that the transfer into the foods is mostly below the detection limit (varying between 10–100 μ g/kg, depending on interfering food components).

Nine (four from 1999) of the most critical products were analyzed, namely vegetables in oil. All lids contained NOGE. One of the packed foods contained 220 μ g/kg of NOGE and its chlorohydrins <1000 Dalton, which was the highest result obtained so far (from some 30 samples analyzed in different surveys). In the other eight products, NOGE concentrations were below 100 μ g/kg.

Key points

The results of the survey may be summarized by the following points.

- 1. Only four out of the 101 canned products analyzed violated Swiss regulations. Assuming that the two thirds of non-controlled (non-critical) cans really met the requirements, this represents less than 1.5% of the canned products. This is a strong improvement compared to the previous campaigns.
- 2. Two of the four products violated the European 1 mg/kg limit for BADGE and its derivatives. The EU regulation for NOGE is in preparation. National regulations in the EU member states vary.
- 3. Over 90% of all products contained less than 200 μ g/kg of BADGE, NOGE and their chlorohydrins, i.e. those exceeding the restrictions were exceptions, rather than the tip of an iceberg.
- 4. Focussing on the critical products, the analysis of some 100 samples achieved a fairly complete control of the market.
- 5. Initially the improvement on the Swiss market was principally achieved through screening of the products. In the mean time, industry has improved their coating systems. It would be of high interest to obtain analogous results from other European markets in order to compare the importance of the two actions.

- 6. It seems that the manufacturing of 2-piece cans and easy open lids does not necessarily require the use of organosol coatings: 56% of the easy open lids and 75% of the deep-drawn cans did not contain PVC.
- 7. BADGE or NOGE were detected in only six of 22 organosol coatings. This indicates that industry moves away from BADGE and NOGE as stabilizers for organosols. The substitutes are still unknown. It remains to hope that the replacements were selected after careful evaluation of safety.
- 8. Migration from the lid into products in glass jars is lower than that into canned products. The European coating industry has decided to phase out the use of NOGE also for lids of glass jars.

Summary

101 samples of the most critical canned products and nine samples in glass jars with twist-off lids were checked for the BADGE and NOGE components with epoxy and/or chlorohydroxy functions. Only four of them violated Swiss regulations, two because of the corresponding BADGE components exceeding the 1 mg/kg limit (3.6 and 4.2 mg/kg) and two because of the presence of NOGE (1 and 5.6 mg/kg). These products were clear exceptions (no other canned product was nearly as seriously contaminated) and represented a minor share of the market. Only few cans had an organosol coating, and most organosols were stabilized neither with BADGE nor NOGE.

Zusammenfassung

101 Proben der aus früheren Untersuchungen als kritisch eingestuften Dosenkonserven und neun Produkte in Gläsern mit Twist-off Deckeln wurden auf BADGE- und NOGE-Komponenten mit einer Epoxy- und/oder Chlorhydroxy-Funktion analysiert. Nur vier davon verstiessen gegen die Schweizer Regelungen: Zwei Produkte enthielten mehr als 1 mg/kg der entsprechenden BADGE-Komponenten (3,6 und 4,2 mg/kg) und zwei das unerlaubte NOGE (1 und 5,6 mg/kg). Es handelte sich um klare Ausnahmen (keine andere Probe war auch nur annähernd ähnlich stark belastet) und um Produkte mit geringem Volumen auf dem Markt. Nur wenige Dosen enthielten einen Organosolinnenlack, und nur wenige Organosole waren mit BADGE oder NOGE stabilisiert.

Résumé

Les composés du BADGE et du NOGE contenant des groupes époxy et/ou chlorohydroxy ont été analysés dans 101 échantillons de conserves en boîtes considérées comme critiques dans des études précédentes et dans neuf échantillons de pots en verre munis d'un couvercle de type "twist-off". Seulement quatre de ces échantillons ne respectaient pas les exigences suisses: deux contenaient plus de 1 mg/kg de composés du BADGE (3,6 et 4,2 mg/kg) et deux autres du NOGE, substance non autorisée (1 et 5,6 mg/kg). Il s'agit clairement d'exceptions, tant par le niveau de la contamination (élevé comparativement aux autres échantillons) que par la part de marché anecdotique des produits en question. Une petite partie seulement des boîtes possédaient un vernis organosol et peu de ces derniers étaient stabilisés avec du NOGE ou du BADGE.

Key words

Canned foods, Bisphenol A diglycidyl ether (BADGE), Novolac glycidyl ether (NOGE), Organosol coatings, Food survey

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