

Interaction of a Vinylic Organosol Used as Can Coating with Solvents and Food Simulants

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Metal cans are often protected from corrosion by vinylic organosol coatings, made from PVC and epoxyphenolic (EP) resins. Using electron spin resonance, BADGE, a monomer of EP, was shown to plasticize PVC. Optimization of extraction allowed extraction of 4 mg of BADGE/dm², so vinylic organosols appear to be worst-case coatings. Comparison of behavior between BADGE and a paramagnetic probe revealed that these compounds were trapped to a large extent in the cross-linked EP network and could not migrate at 40 °C. Contact with triglycerides, which plasticize the coating, induced high migration of BADGE. Neither isooctane nor ethanol could mimic fats, in contrast to isooctane/*tert*-butyl acetate mixtures. In aqueous foodstuffs, BADGE hydrolyzed into a monoepoxide and then into a bisdiol. The total amount of toxicologically relevant epoxides over shelf life was shown to reach a maximum value within 3 weeks at 40 °C, at very low levels, whatever the aqueous food simulant. After sterilization at 120 °C (20 min), the level of BADGE in the migrate is very low, whereas up to 2 mg of hydrolysis products is found in the liquid/dm². During further storage at 40 °C, the amount of epoxides rapidly decreases.

INTRODUCTION

Epoxy compounds, such as bisphenol A diglycidyl ether (BADGE), are used as cross-linking agents for coatings and varnishes. Any unreacted epoxy compound in the inner coating of cans may migrate into foodstuffs. In the past, the Scientific Committee for Food (SCF) estimated that all epoxides should be nondetectable in foodstuffs, which was equivalent to a specific migration limit of 20 µg/kg of food. More recently, the SCF received toxicological data showing that BADGE, the most used epoxy cross-linker, was not mutagenic *in vivo*, due to a rapid metabolic detoxification by hydrolysis of the epoxy functional groups (SCF 1996). A specific migration limit of 1 mg/kg of food was allocated to BADGE together with some reaction products. Analytical determinations in cans revealed that this value was exceeded in a small number of canned food samples. Among the many formulations used, vinylic organosols appeared to be the main substance responsible for these high migration levels (Biedermann et al., 1996).

Vinylic organosols belong to the coatings that have the highest chemical inertness (Vaz de Faria, 1987). They are therefore widely used for the most aggressive foodstuffs and prevent efficiently the corrosion of the underlying metal. Vinylic organosols are manufactured by mixing several types of resins: poly(vinyl chloride) (PVC), epoxy resins, and phenolic and epoxyphenolic (EP) resins (Trotignon et al., 1988), which form after curing a network.

In the first part of this work, using a grafted paramagnetic probe, we have shown that the mobility of PVC

chains and of EP could be observed independently by electron spin resonance (ESR) and that they were not ruled by the same factors (Cottier et al., 1996, 1997a). This approach is now extended to investigate structural changes of the coating in the course of migration of BADGE into food simulants.

The first objective of the present paper is to provide an understanding of the behavior of BADGE in vinylic organosols during contact with food and to contribute to the formulation of new vinylic organosols with a reduced BADGE migration.

The second objective is to predict the influence of coating cure, of food sterilization, and of food type on migration.

MATERIALS AND METHODS

Coatings and Chemicals. Vinylic organosol, a liquid resin, was applied to aluminum sheets (20 µm) using a spinning wheel at 2850 rpm for 3 s. Under standard flash cure conditions (normal), the coating was heated for 20 s in an oven, to reach a peak metal temperature of 250 °C (PMT₂₀ = 250 °C). In undercured and overcured resins, the heating times, were respectively, 15 and 25 s. The coating was then separated from the aluminum foil by immersion in a solution of mercuric chloride (8%) for 15 min, followed by thorough rinsing with cold water.

Liquid resins containing either twice the usual amount of BADGE or one-third of it were cured as above. Coatings were also prepared on tin plates, using the same procedure. The vinylic organosol was then removed from the metal using the mercury method (Cottier et al., 1996).

BADGE (95% purity) was obtained from CIBA (Basel).

Simulants and test media were as follows: aqueous simulants, water (MilliQ), 3% acetic acid (Merck), and 15% ethanol (Prolabo); fatty simulants, olive oil (PIRA, Leatherhead, U.K.) and a commercial mixture of C₈/C₁₀ triglycerides (Miglyol 812, Hüls, Puteaux, France); solvents, isooctane (ISO) (Prolabo),

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Table 1. Different Analytical Conditions for Separation of the Potential Migrants of the Coating

analytical conditions	experiments	injection (μL)	flow rate (mL min^{-1})	mobile phase	calibration of detector
1	extracts	10	0.8	isocratic elution, $\text{CH}_3\text{CN}:\text{H}_2\text{O}^a$ (50:50)	1
2	migrates in water or in olive oil	20	1.5	$\text{CH}_3\text{CN}:\text{H}_2\text{O}$ isocratic elution 25:75 for 5 min gradient from 25:75 to 50:50 in 10 min isocratic elution 50:50 for 30 min gradient from 50:50 to 100:0 in 15 min	200
3	migrates in oil or in solvents	20	1.5	$\text{CH}_3\text{CN}:\text{H}_2\text{O}$ isocratic elution 25:75 for 5 min gradient from 25:75 to 50:50 in 10 min isocratic elution 50:50 for 30 min gradient from 50:50 to 100:0 in 15 min	

^a $\text{CH}_3\text{CN}:\text{H}_2\text{O}$, binary mixture of acetonitrile and water.

tert-butyl acetate (TBA) (Aldrich), and ISO/TBA mixtures ranging from 5 to 50% TBA in isooctane.

Extraction of BADGE from the Coating. Coated sheets (17.6×10 cm), prepared as described above, were extracted in a Soxhlet by methanol (100 mL). The weight of the coating was measured before and after extraction. The extract was monitored by GC or UV, until a plateau was reached (constant peak areas or constant absorbance). The 1 mm quartz UV cells were supplied by Hellma (Paris labo, Paris). The UV spectrometer was a UV-vis Uvikon 941 (Kontron Instruments).

Analysis of BADGE by High-Performance Liquid Chromatography (HPLC). The liquid chromatograph (Varian 5000) was connected to a spectrofluorometric detector (SFM 25, Kontron Instruments). The column was a Lichrospher C8 (Interchim, Montluçon, France) (250×4.6 mm, $5 \mu\text{m}$ granulometry) equipped with a 1 cm C18 Lichrospher guard column ($5 \mu\text{m}$ granulometry). The chromatograms were processed using Borwin software (JMB Developpements, Le Fontanil, France). The different analytical conditions for separation of the potential migrants of the coating are given in Table 1. Calibration was carried out by injecting commercial BADGE as a methanol solution for each of the conditions specified in Table 1. The detection limits were $20 \mu\text{g L}^{-1}$ for conditions 2 and 5 mg L^{-1} for conditions 1 and 3.

Migration Experiments. In all migration experiments, there was a single-side contact of the film with the simulant. The ratio (volume of simulant/area of film) was always 0.166 dm, corresponding to the European Unions's (EU) standard test conditions (European Union, 1997). Two sets of conditions were used: 10 days at 40°C , in a thermostated oven ($\pm 0.1^\circ\text{C}$) [the coating was immersed (0.150 dm^3 of food simulant) in a tightly closed jar without being removed from its aluminum support]; 20 min at 120°C [food simulants were heated directly in the cans (2); the area of film in contact with the simulant was 0.9 dm^2].

Analysis of Simulants. After contact, the solvents were evaporated to dryness and the residues dissolved in methanol (10 mL). The methanol solution was directly injected. It was checked that evaporation to dryness had no influence on the recovery of BADGE, by two successive evaporation to dryness-redilution cycles.

The aqueous simulants (water, 3% acetic acid, 15% ethanol/water) (150 mL) were extracted on a C18 solid-phase column (Sep-Pak, Waters, WAT 020515) and then desorbed by methanol (3 mL) (Paseiro Losada, 1993). The methanol solution was analyzed by HPLC (conditions 2).

Olive oil (150 mL) was extracted twice with acetonitrile (2×150 mL). The acetonitrile phase was washed with hexane (30 mL), evaporated almost to dryness. The residue was dissolved in 10 mL of methanol for the migrations carried out for 10 days at 40°C and then injected in HPLC in conditions 2 (concentration factor of 15); or 5 mL of methanol for the migrations carried out for 20 min at 120°C and then injected in HPLC in conditions 3 (concentration factor of 30).

Hydrolysis of BADGE. A solution of BADGE (0.02 mg/mL) in tetrahydrofuran (1 mL) was diluted in 50 mL of aqueous simulant: water, 3% acetic acid, or 15% ethanol.

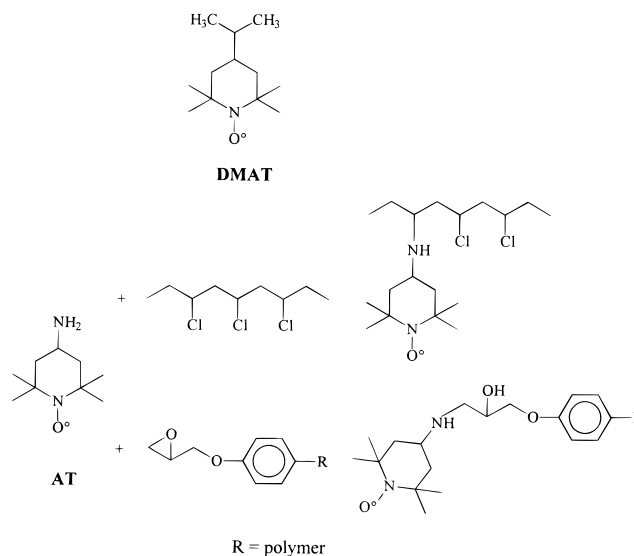


Figure 1. Paramagnetic probes DMAT and AT; grafting of AT on PVC and on EP during cure.

Samples were taken at regular intervals during 10 days at 40°C and analyzed by HPLC (conditions 2).

Differential Scanning Calorimetry (DSC). Glass transition (T_g) temperatures were measured on a DSC TA 3000 Mettler with a TC10 processor connected to a print Swiss Matrix recorder. The samples (9–12 mg) were analyzed under the following conditions: initial temperature, 30°C ; final temperature, 150°C ; heating rate, $20^\circ\text{C min}^{-1}$; cooling with a flow of liquid nitrogen. The T_g values were measured in the second run by the midpoint method.

ESR Studies. The spin probes used were 4-(*N,N*-dimethylamino)-2,2,6,6-tetramethylpiperidin-1-oxyl (DMAT) (Figure 1), synthesized according to reported procedures (Hamdani et al., 1995), and 4-amino-2,2,6,6-tetramethylpiperidin-1-oxyl (AT), which is grafted during cure at chain ends (Figure 1) (Cottier et al., 1997a). These probes (750 ppm) were added separately to the normal formulation of the coating, before cure (Cottier et al., 1997a).

Spectra were measured and recorded at 10 mW with an ESP 300 (9.6 GHz) spectrometer (Bruker, Wissembourg, France), controlled by an ESP 1620 calculator. Spectra were measured in the temperature range between 30 and $160\text{--}175^\circ\text{C}$ using a variable temperature unit (Bruker ER 4111 VT). Spectra were recorded with an amplification of 4×10^4 for samples spin labeled by AT and an amplification of 1.25×10^5 for samples spin labeled by DMAT. Spectral intensities were evaluated from the second integral of the first derivative spectrum.

Conditions of contact for ESR studies were as follows: the films containing AT were placed for 3 and 10 days at 40°C in 25 mL bottles containing aqueous simulants, fatty simulants, or solvents. The films were then dried on absorbant paper and placed in the NMR tubes (5 mm) for ESR

analysis. Migration was determined using the following relationship:

$$\% \text{ migration of probe} = \frac{\text{spectral intensity before contact} - \text{after contact}}{\text{spectral intensity before contact}} \times 100$$

Confocal Microscopy. The depth of penetration of the simulants in the coating was measured with a CLSM 310 Carl Zeiss confocal laser scanning microscope equipped with ion-argon lasers (excitation wavelength = 488 nm) and helium-neon lasers (excitation wavelength = 543 nm). The images were processed with Carl Zeiss LSM software. A 40 lens was used to visualize the surface of the coating as well as the penetration of the contact medium.

Measurements were taken with a contrast of 400 and a brightness of 900. The simulants (miglyol, olive oil, and mixtures ranging from 5 to 50% of *tert*-butyl acetate in isooctane) contained succidinimidyl 6-(7-nitrobenz-2-oxa-1,3-diazol-4-yl) aminohexanoate (10^{-6} M) as fluorescent probe.

After contact, the films were wiped, cut into approximately 5 mm × 5 mm × 0.015 mm pieces, and placed between a slide and cover slip before being analyzed.

Calculations. All kinetics considered were of first order. For a transformation $X \rightarrow Y$:

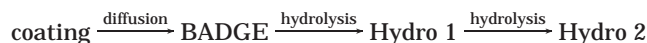
$$-dX/dt = dY/dt = kx$$

No mathematical resolution of this type of reaction was undertaken because in our case successive physical (diffusion) and chemical (hydrolysis) phenomena had to be considered. Changes of the product concentrations were calculated step by step with short time increments = $dx/dt \approx \Delta x/\Delta t$.

The quantities of chemical species having diffused or formed by reactions between two time increments were evaluated by an approached resolution of Fick's equation [$F(t)$].

Considering the mechanism

Scheme 1



the following equations are obtained:

$$\Delta[\text{BADGE}]_t = -k_1[\text{BADGE}]_{t-\Delta t}\Delta t + F(t) - F(t - \Delta t)$$

$$[\text{BADGE}]_t = [\text{BADGE}]_{t-\Delta t} + \Delta[\text{BADGE}]_t$$

$$\Delta[\text{Hydro 1}]_t = k_1[\text{BADGE}]_{t-\Delta t}\Delta t - k_2[\text{Hydro 1}]_{t-\Delta t}\Delta t$$

$$[\text{Hydro 1}]_t = [\text{Hydro 1}]_{t-\Delta t} + \Delta[\text{Hydro 1}]_t$$

$$\Delta[\text{Hydro 2}]_t = k_2[\text{Hydro 1}]_{t-\Delta t}\Delta t$$

$$[\text{Hydro 2}]_t = [\text{Hydro 2}]_{t-\Delta t} + \Delta[\text{Hydro 2}]_t$$

$F(t)$ is the cumulated BADGE concentration, obtained by diffusion

$$F(t) = [\text{BADGE}]_{t=\infty} \left[1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2} \exp \frac{-Dt^2(2n+1)^2}{4L^2} \right]$$

D = diffusion coefficient of BADGE, L = film thickness, and k_1 , k_2 = hydrolysis rate constants of BADGE and Hydro 1, respectively.

RESULTS

To draw a complete picture of the interaction of food simulants with packaging materials, it is essential to correlate structural changes induced in the polymer by the penetration of the liquid. In this work, local free

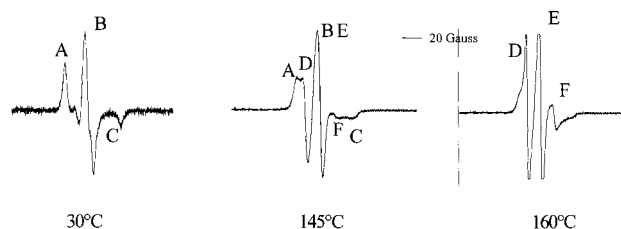


Figure 2. ESR spectra of a vinylic organosol (normal cure) at different temperatures; lines D–F describe the mobility of the probe AT in the PVC phase of the organosol (T_{FS}); lines A–C describe the mobility of the probe AT in the EP phase of the organosol (T_{50G}).

volume variations were monitored by ESR, using aminoxyls as paramagnetic probes. Plasticization effects were studied by DSC. The penetration of liquids was observed using fluorescence confocal microscopy. Migration of BADGE was correlated to that of a paramagnetic probe.

Paramagnetic probes have been widely used to study transitions in polymers. They can be either dispersed in the polymeric matrix or covalently bound to polymer chains (Cameron et al., 1989). In the field of food and packaging interactions, aminoxyls can be used as model additives (Riquet and Feigenbaum, 1997). It is then possible to specifically detect the probe in the polymer and to observe local changes in free volume. Complementary analysis of the food simulant allows us to monitor their migration. In this work we used two probes, DMAT, which can be dispersed in the polymeric matrix (Figure 1), and AT, which can be either dispersed or grafted onto PVC and EP during the cure (Cottier et al., 1996) (Figure 1). In conditions used here, >80% AT was grafted (measured by comparison with a fully grafted PVC sample). Therefore, AT was used for investigation of the structure, whereas DMAT-containing materials were used for migration studies.

Influence of Cure on the Transitions of Vinylic Organosol. Transitions of EP phases may be observed at temperatures >200 °C. Using our ESR variable temperature unit (maximum temperature = 180 °C) did not enable reaching this temperature range. Consequently, we focus mainly on the PVC phase. In coatings cured normally, and containing grafted AT, two environments with two distinct transitions have been observed by ESR (Figure 2). The first one, called T_{FS} , in the 140–145 °C range, has been related to the glass transition of PVC (Cottier et al., 1996). The second one, called T_{50G} , observed at 155–160 °C, corresponded to the mobility of EP chain ends (Cottier et al., 1997).

At temperatures between T_{FS} and T_{50G} , the ESR spectrum of the coating appears as a superimposition of two spectra, corresponding to PVC and EP environments (Figure 2). Glass transition temperatures (T_g), T_{FS} , and T_{50G} increase with the extent of curing (Table 2, entries 1–3). In the overcured coating, both T_{FS} and T_{50G} exceeded the highest temperature possible with the instrument (175 °C) and could not be observed.

This increase of the transition temperatures reflected a reduced mobility of the probes in the PVC (T_{FS}) and in the EP (T_{50G}) phases. This could be explained in several ways. A first hypothesis was that PVC chains were entangled in the EP tridimensional network, as cross-linking increases with the extent of cure. Another hypothesis was that there are in the PVC phase molecules (possibly BADGE) which have a plasticizing

Table 2. T_g , T_{FS} , and T_{50G} of Vinylic Organosols Made from Different Percentages of BADGE and with Different Extents of Cure, before (c) and after (d) Extraction^a

entry	cure	amount of BADGE		T_g (°C)		T_{FS} (°C)		T_{50G} (°C)	
		a	b	c	d	c	d	c	d
1	undercured	1	7.4	65	90	135	155	150	
2	normal cure	1	4	76	90	145	160	155	
3	overcured	1	2.3	82	90	>180	>180	>180	
4	undercured	0.6		72	88	140	155	165	
5	normal cure	0.6		73	89	140	160	175	
6	overcured	0.6		80	90				
7	undercured	2		60	87	125	160	155	
8	normal cure	2		63	90	130	160	152	
9	overcured	2		76	90				

^a a, relative amount of BADGE initially introduced in the formulation; b, amount of BADGE (mg/dm²) extracted after cure.

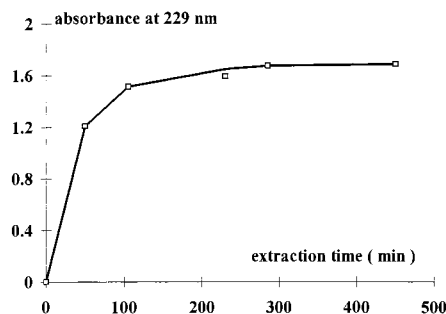


Figure 3. Kinetic of extraction of BADGE from the coating by Soxhlet with methanol (UV analyses).

effect and which would react during cure. Therefore, the influence of the initial amount of BADGE was studied.

Influence of the Initial Amount of BADGE. Coatings labeled with AT were cured with 0.66, 1, and 2 times the usual amount of BADGE. Results presented in Table 2 confirm that whatever the initial amount of BADGE, transition temperatures increased with the extent of cure. Furthermore, there is a general trend: whatever the extent of cure, T_{FS} and T_g decreased as the initial amount of BADGE increased (Table 2, entries 1, 4, 7; entries 2, 5, 8; entries 3, 6, 9). T_{FS} and T_g thus appeared as indicators of the evolution of the PVC phase, which was plasticized by BADGE. In contrast, T_{50G} was not closely related to the initial amount of BADGE (Table 2).

Influence of Extraction. BADGE was extracted from all vinylic organosol films studied in the previous two sections by methanol, using a Soxhlet instrument. Results are shown in Table 2. Extraction of BADGE was optimized by monitoring the absorbance of extracts at 229 nm (Figure 3). A plateau was reached within 200 min.

After extraction, T_g and T_{FS} strongly increased. They reached almost the same value ($T_g = 90$ °C; $T_{FS} = 160$ °C) whatever the extent of cure and the initial amount of BADGE (Table 2, entries 1–3). This confirmed that the main reason for the changes in these transition temperatures with cure was the level of residual BADGE, rather than differences in cross-linking.

Migration of DMAT and BADGE. Coatings containing DMAT in addition to the normal formulation were submitted to migration tests. DMAT was monitored by ESR and BADGE by liquid chromatography (Cottier et al., 1997). Two sets of temperatures were

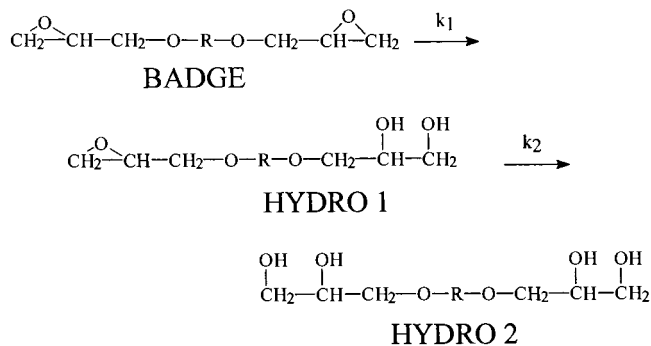


Figure 4. Hydrolysis of BADGE in aqueous media.

tested: 40 °C (10 days), representing long-term storage at room temperature; and 120 °C (20 min), simulating the sterilization step. The test media were the official aqueous and fatty simulants (European Union, 1997) as well as solvents. Because BADGE is known to hydrolyze in aqueous media (Paseiro Losada et al., 1993; Philo et al., 1997), we decided to determine the kinetic constants for the formation of hydrolysis products.

Hydrolysis of BADGE in Aqueous Media. Hydrolysis of BADGE in aqueous media results mainly in monoepoxide Hydro 1, which is then transformed into the bisdiol Hydro 2 (Figure 4). The latter compound bears no more epoxide group and is stable in these media. Furthermore, rate constants were reported only for the first hydrolysis step, whereas the second hydrolysis step is also essential for safety assessment of the coatings (Paseira Losada et al., 1992; Philo et al., 1997). We therefore determined the hydrolysis kinetics of BADGE in aqueous media (Figure 5). Only the reaction kinetics of BADGE with water is displayed here. In water at 40 °C, BADGE disappeared completely after 8 days. In the other simulants, BADGE disappeared even more rapidly. Only the two hydrolysis products could be detected after 10 days, whatever the medium.

To determine k_1 and k_2 from experimental data, master curves were drawn, assuming pseudo-first-order kinetic laws for reactions 1 and 2 (Figure 5):



This corresponded to the following equations:

$$d[\text{BADGE}]/dt = -k_1[\text{BADGE}] \quad (1)$$

$$d[\text{Hydro 1}]/dt = k_1[\text{BADGE}] - k_2[\text{Hydro 1}] \quad (2)$$

$$d[\text{Hydro 2}]/dt = k_2[\text{Hydro 1}] \quad (3)$$

k_1 and k_2 were obtained from the best fit of the master curves with experimental values. k_1 thus determined was close to values reported by other authors (Paseiro Losada et al., 1993; Philo et al., 1997) (Table 3). It can be seen from Table 3 that k_2 is approximately $k_1/2$, as could be expected.

Migration of BADGE into Aqueous Media. Migration of BADGE was determined at 40 °C (10 days) and at 120 °C (20 min). Values are reported in mg of BADGE/dm² of coating (Table 4) and as percentage of BADGE extractable by Soxhlet with methanol (Table 5) (Cottier et al., 1997).

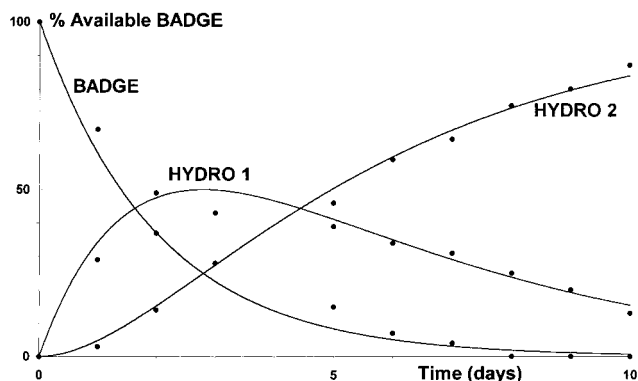


Figure 5. Kinetics of hydrolysis of BADGE into Hydro 1 (k_1) and into Hydro 2 (K_2) in water.

Table 3. Kinetic Constants of Hydrolysis of BADGE [a, This Work; b, Paseiro Losada (1993); c, Philo (1997)] in Aqueous Food Simulants

		$t_{1/2}$ (h)	k (h^{-1}) = $\ln 2/t_{1/2}$	k_1 (h^{-1}) \pm 5×10^{-3}	k_2 (h^{-1}) \pm 10^{-3}
water	a	41	0.017	0.019	0.010
	b	43	0.016		
	c	41	0.017		
3% acetic acid	a	8.5	0.081	0.095	0.052
	b	8.1	0.085		
	c	4.2	0.165		
20% ethanol	a	58	0.012	0.014	0.007
	b	69	0.010		
	c	30	0.023		

Table 4. Migration of BADGE (mg/dm^2) from Vinylic Organosols into Aqueous Simulants at 40 °C (10 Days) and at 120 °C (20 min)

aqueous simulant	migration 10 days at 40 °C			migration 20 min at 120 °C		
	water	3% acetic acid	15% ethanol	water	3% acetic acid	15% ethanol
BADGE	0.3×10^{-3}	0.5×10^{-3}	0.7×10^{-3}	ND ^a	ND	ND
Hydro 1	0.5×10^{-3}	1.1×10^{-3}	1×10^{-3}	0.5	0.7	0.4
Hydro 2	2×10^{-3}	1.6×10^{-3}	2×10^{-3}	1	1.5	0.9
total	2.8×10^{-3}	3.2×10^{-3}	3.7×10^{-3}	1.5	2.2	1.3

^a ND, not detected.

The levels of Hydro 1 and Hydro 2 were much higher in sterilization conditions than after 10 days at 40 °C.

At 40 °C, in contrast to the results shown in Figure 5 and with all hydrolysis experiments, some BADGE was detected even after 10 days. The difference between the two sets of experiments most likely arose from the permanent slow release of BADGE from the coating (Scheme 1).

This suggested that hydrolysis of BADGE in the simulants could be partly compensated by its gradual release from the coating at 40 °C. At 120 °C, hydrolysis was much faster, and BADGE reacted as soon as it migrated.

Migration of BADGE into Fatty Simulants. Migration of BADGE into olive oil at 40 °C was not detectable. Due to interferences with compounds of the olive oil used during the chromatographic analysis, the detection limit (50 $\mu\text{g}/\text{L}$) was slightly higher than with other published methods (Biedermann et al., 1996; Tice, 1988). At 120 °C a much higher migration (0.7 mg/dm^2) was observed. This may reflect the large difference in solubilities of BADGE at these two temperatures. No hydrolysis product of BADGE was detected in oil, at both test temperatures.

Table 5. Percentage of Migration of BADGE and of DMAT in Simulants

test medium	specific migration of BADGE (10 days at 40 °C)	specific migration of DMAT (10 days at 40 °C)
water	0.07	1.1
acetic acid	0.08	2
15% ethanol	0.09	
isooctane	0.058	ND ^b
ISO/TBA 90:10	12.5	11.76
ISO/TBA 80:20	17.5	17.6
methanol	20	
ISO/TBA 50:50	52.2	
<i>tert</i> -butyl acetate	52.2	49.4
miglyol		35
olive oil ^a	17.5	

^a 20 min, 120 °C. ^b ND, not detectable.

Table 6. Changes in T_{FS} Parameter of DMAT after Contact with Different Test Media

test medium	T_{FS} (± 5 °C) 3 days at 40 °C
without contact	130
water	130
3% acetic acid	130
20% ethanol	130
isooctane	130
ISO/TBA 80:20	115
ISO/TBA 40:60	no signal for the PVC component
<i>tert</i> -butyl acetate	no signal for the PVC component
olive oil	130
miglyol	120

Migration of DMAT into Miglyol. Migration of DMAT into miglyol was monitored at 40 °C. Miglyol was used rather than olive oil, which may contain compounds reacting with the NO^{*} group of aminoxyls.

Because DMAT largely evaporated during cure, the corresponding ESR signal was weak, and the measurements had a large margin of error ($\pm 10\%$) (Cottier et al., 1996). After 3 days at 40 °C, 35% of the initial amount of the probe had migrated into miglyol. The same value was obtained after 10 days at 40 °C, which suggested that it corresponded to a steady state.

Migration of DMAT and BADGE into Solvents. Due to experimental difficulties linked to the use of olive oil, it is desirable to have alternative test media available. Usually, isooctane or ethanol is used (European Union, 1997). However, these solvents have very extreme polarities, whereas fats have an intermediate behavior; furthermore, ethanol may react with epoxy groups (Philo et al., 1997; Cottier et al., 1997b). We therefore used isooctane/*tert*-butyl acetate mixtures and tailored the aggressivity of the medium by changing the percentage of *tert*-butyl acetate. Results are shown in Table 5. Surprisingly, only 50% of BADGE and DMAT migrated in pure TBA at 40 °C.

Penetration of Fatty Simulants and Test Media in the Vinylic Organosol Coating. Penetration was monitored in two ways: using coatings labeled with DMAT, it was possible to observe differences in T_{FS} , which were related to local changes in the free volume associated with the presence of solvent molecules; using confocal microscopy and a fluorescent probe.

Changes in T_{FS} after Contact with Lipophilic Media. The coating was analyzed after contact for 3 days at 40 °C with isooctane/*tert*-butyl acetate mixtures (ISO/TBA) (Table 6).

Isooctane had no effect on T_{FS} . When the percentage of *tert*-butyl acetate in isooctane increased, T_{FS} decreased. When the percentage was $>40\%$, there no

longer was a signal for the PVC component: the entire probe located in the PVC environment had migrated and T_{FS} could not be measured anymore. The residual signal present corresponded exclusively to the EP environment, where DMAT molecules seemed to be trapped. The same spectrum was observed with pure TBA. This suggested that at 40 °C, these solvents could have access to DMAT and BADGE molecules only in the PVC environment.

Penetration of Fatty Simulants by Confocal Microscopy. Using confocal microscopy, the penetration of test media and of solvents likely to interact with the coating was studied: ISO/TBA mixtures, miglyol, and olive oil.

The penetration of these media could be seen as a sharp boundary (Feigenbaum et al., 1991). After 10 days at 40 °C, the penetration depth increased with the percentage of TBA. With percentages of TBA $\geq 40\%$, there was complete penetration of the film by the solvent. The penetration depth of miglyol was closed to that of the ISO/TBA (80:20) mixture.

DISCUSSION

Structure of the Coating before Contact with Food Simulants. By DSC analysis of the coating, a single transition is observed, which indicates a homogeneous material, whereas by ESR, two distinct transitions can be seen. This most likely corresponds to local effects in the environment of the probes (Bullock 1984). AT molecules can graft either on PVC chains (in-chain grafting) or on epoxy groups of a terminal epoxy moiety (Figure 1). In the latter case, the probe is at the chain end of a cross-linked polymer and has a slightly greater mobility than in chain segments or side groups (Figure 1). We here use the expressions PVC phase and EP phase, and these should be understood at local levels.

By extraction of the coatings, all transition temperatures increase and reach similar values for undercured and normally cured coatings. This shows that BADGE and derivatives behave as a plasticizer of the coating. This could explain why it was used in such a large excess (Cottier et al., 1997). Vinylic organosols are used when the coating is submitted to strong constraints, as for two-piece cans or easy-to-open lids (Biedermann et al., 1996). The large excess of BADGE is also justified by its function as a stabilizer, reacting with hydrogen chloride during cure (Cottier et al., 1997b).

Solvent-Coating Interactions. DMAT and BADGE display very similar tendencies to migration into lipophilic media. Because their functional groups are different, this probably reflects the interaction between the coating and the solvent.

At 40 °C, isooctane is not aggressive toward the coating and leads to very slight migration. The same behavior has been observed with rigid PVC bottles as isooctane does not interact with the polymer (Riquet et al., 1995/96, Cottier et al., 1996). Food fats such as miglyol penetrate into the coating and plasticize it, as can be seen by the drop in T_{FS} during contact (Table 6). This plasticization effect is related to ester functional groups of the triglycerides.

Mixtures of *tert*-butyl acetate and isooctane are more aggressive than isooctane alone: the larger the percentage of *tert*-butyl acetate (up to 50%), the larger the migration of DMAT and of BADGE. Around 50% of the available DMAT migrated after 3 days in an isooctane/TBA (1:1) mixture. The DMAT signal in the PVC phase of the coating completely disappears while DMAT is still

present in EP environments. When the aggressivity of the extractant is $> 50\%$, as with pure *tert*-butyl acetate, the same results are obtained. At 40 °C the solvents can extract only 50% of the total available BADGE, as well as 50% of the total available DMAT. Furthermore, the solvents can extract DMAT only from the PVC phase (the signal selectively disappears in the coating) and not from the EP phase. Fifty percent of DMAT molecules are trapped in cross-linked areas of the coating and cannot migrate or be extracted in these conditions.

This could explain the behavior of BADGE, the migration of which parallels that of DMAT. At 40 °C, the amount transferred in solvents never exceeds 50% of the amount of DMAT that can be extracted by hot methanol in a Soxhlet. It is likely that at 40 °C, a high proportion of BADGE remains trapped in the EP phase and is not accessible to solvents and food simulants, whatever their aggressivity for the PVC phase. At higher temperatures, close to the boiling point of methanol, as in Soxhlet extraction, a very efficient extraction can be carried out. This is a further example of accessibility effects of solvents into polymeric matrices (Feigenbaum et al., 1997).

By the addition of *tert*-butyl acetate to isooctane, its aggressiveness is increased. The ester has a plasticizing effect similar to that of food fats. This illustrates how a fatty food simulant can be tailored by using a mixture of an ester with a noninteracting solvent, in the case isooctane (Riquet and Feigenbaum, 1997).

The migration of BADGE in olive oil at 40 °C is very low (not detectable), due to its poor solubility (5 mg/L at 100 °C). However, cans are usually sterilized at higher temperature, and this strongly stimulates migration by improved solubilization.

A mixture of isooctane and *tert*-butyl acetate (4:1) for 3 days at 40 °C behaves like olive oil for 20 min at 120 °C. As far as migration of BADGE in oil is concerned, it is not important to have an alternative test available: BADGE is polar and can be easily separated from oil by extraction (Tice, 1994; Biedermann et al., 1996; Cottier et al., 1997). However, other compounds are present in the coating, and it may be useful to have an alternative test medium available. Alternative tests are much more convenient to carry out than migration tests because they do not require extraction steps of BADGE from oil.

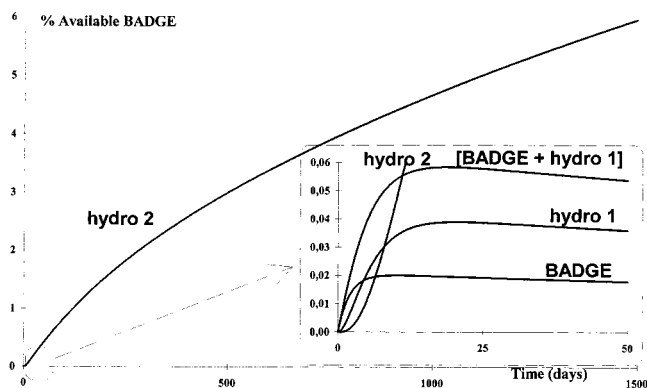
The two official media replacing fats in substitute tests are not adequate: isooctane does not interact with the coating, and ethanol reacts with the migrants by addition reactions (Philo et al., 1997). The isooctane/*tert*-butyl acetate mixture optimized here is therefore the only suitable test medium for vinylic organosols. Such mixtures are now accepted as alternative test media (European Union, 1997).

Safety Assessment of Vinylic Organosols and Epoxy Coatings Taking into Account Hydrolysis of BADGE and Hydro 1. In simple situations, the concentration of the migrant in foodstuffs increases with square root of time, up to 60% migration. Testing at 10 days thus enables extrapolation of worst-case migration values after 1 year. The picture is more complicated here: on the one hand, BADGE disappears from the simulants by hydrolysis (reactions 1 and 2); on the other hand, its hydrolysis product Hydro 1 is also relevant for safety assessment.

After 10 days at 40 °C, some BADGE was present in migration experiments with aqueous simulants but no

Table 7. Highest Possible Levels of BADGE, Hydro 1, and Epoxides (BADGE + Hydro 1) in Migration Test into Aqueous Simulants at 40 °C

conditions	BADGE		Hydro 1		epoxides	
	time to max (days)	highest level ($\mu\text{g}/\text{dm}^2$)	time to max (days)	highest level ($\mu\text{g}/\text{dm}^2$)	time to max (days)	highest level ($\mu\text{g}/\text{dm}^2$)
3% acetic acid	3.00	0.081	6.10	0.161	5.70	0.242
water	10.20	0.400	20.50	0.778	18.90	1.168

**Figure 6.** BADGE, Hydro 1, Hydro 2, and [BADGE + Hydro 1] from migration experiment in water at 40 °C.

BADGE was detected in hydrolysis experiments. This suggested that BADGE was constantly supplied to the simulant by migration. Knowing k_1 and k_2 and having migration experiments available, it is possible to predict the concentration of BADGE and the sum [BADGE + Hydro 1] for long-term storage.

From migration experiments at 10 days (Table 4), apparent diffusion coefficients of BADGE could be calculated by assuming a constant diffusion coefficient, which is justified because the aqueous simulants have limited plasticizing effects (Table 6). The determination of D values was facilitated because we had to fit the three curves for BADGE, Hydro 1, and Hydro 2 concentrations knowing k_1 and k_2 from previous hydrolysis experiments (Table 3).

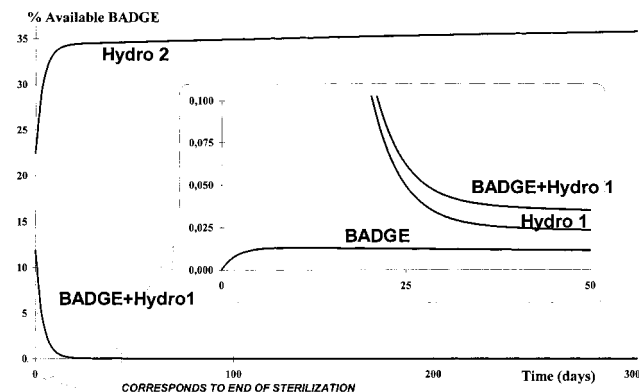
The fitting of experimental values with calculated curves is shown in Figure 6 in the case of migration with or without sterilization. The total amount of available BADGE was 2 mg/dm^2 at 40 °C and 4 mg/dm^2 at 120 °C. The apparent diffusion coefficient ($D = 6.7 \times 10^{-17} \text{m}^2 \text{s}^{-1}$ in water) in fact includes both the diffusion in the polymer and the partition between the varnish and the simulant at the interface. We have also displayed in this figure the total amount of epoxides [(BADGE) + (Hydro 1)], a factor that is relevant from the toxicological point of view (SCF 1996).

The following results are obtained.

(i) Packaging and Long-Term Storage at Room Temperature. The official testing temperature is here 40 °C. BADGE, Hydro 1, and [(BADGE)+(Hydro 1)] go through a maximum that is always reached within 10 days at 40 °C. Coordinates of these maxima are reported in Table 7.

(ii) Sterilization, followed by Long-Term Storage. Immediately after retortion as shown in Figure 7, there are important levels of Hydro 1 present in the simulant (Table 4). However, when the vinylic organosols are stored for longer times in contact with these aqueous media at 40 °C, the epoxides decrease and rapidly reach very low levels (Figure 7).

This definitely shows that hydrolysis is always fast enough to decrease the level of BADGE to acceptable levels in homogeneous aqueous media.

**Figure 7.** Migration of BADGE, Hydro 1, and Hydro 2 in water after sterilization (20 min at 120 °C) and then at 40 °C.

CONCLUSION

BADGE strongly plasticizes the PVC phase of the coating, as shown by DSC studies. By ESR it is possible to differentiate PVC and EP environments and to show that the main effect is on the PVC phase.

A picture of the interaction of vinylic organosols with simulants has been drawn by complementary approaches. Extraction of BADGE could be related to that of DMAT. At 40 °C, only 50% of the available BADGE or DMAT can be transferred into simulants (olive oil, miglyol), into alternative test media (isooctane/*tert*-butyl acetate mixtures), or in extraction solvents (*tert*-butyl acetate). ESR showed that the DMAT molecules which could not be extracted were trapped in the EP network.

Extraction of BADGE together with all of the other aromatic potential migrants has to be carefully optimized as a function of both time and temperature. It is very convenient to monitor the extraction of BADGE by UV spectrometry. At ≤ 40 °C, extraction solvents have access only to the PVC phase. A complete extraction requires higher temperatures.

Migration diffusivities and hydrolysis rate constants in aqueous simulants have been determined to simulate long-term storage. Because all of the kinetics are first order, percentages of migration do not depend on the initial amount of BADGE and the master curves in Figures 6 and 7 are of general application. The coating studied here can be regarded as a worst case, because of its very high BADGE content. This will increase both absolute migration values and the diffusion coefficient in aqueous simulants due to the plasticization effects. BADGE and the sum [BADGE + Hydro 1] are not likely to exceed the specific migration limit. This contrasts with the fact that high levels of BADGE have been detected in real foods with a large water content (Biedermann et al., 1996). As already suggested by Biedermann, the other phases present in foods (fat, proteins...) protect the epoxides from hydrolysis.

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