**INTRODUCTION**

One of the ways of the can inner coating preservations employs varnishes based on epoxy resins or vinylic organosols. These resins can be produced from bisphenol A (BPA) and bisphenol F (BPF) and they also contain bisphenol A diglycidyl ether (BADGE) or bisphenol F diglycidyl ether (BFDGE) as stabilising components. These compounds may break down during storage and also by influence of food simulants. The stability of BADGE and BFDGE was studied using reverse-phase gradient high performance liquid chromatography (RP-HPLC) with fluorescence detection (FLD). Four experiments were compared: (i) BPA solution at the concentration 3 µg/ml of each food simulant, (ii) BADGE solution at the concentration 3 µg/ml of each food simulant, (iii) BFDGE solution at the concentration 3 µg/ml of each food simulant and (iv) mixture of all bisphenols solution at the concentration 3 µg/ml of each food simulant. Distilled water, 10% ethanol, 95% ethanol and 3% acetic acid were used as food simulants. It was observed that BPA, BADGE and BFDGE were most stable in 95% ethanol and least stable in 3% acetic acid. Creation of hydroxy and chlorohydroxy derivatives was in each food simulant different so it cannot be predicted.

**Keywords**: bisphenols; hydroxy and chlorohydroxy derivatives; food simulants; migration; liquid chromatography
limit is the same as in the case of BADGE. The use and/or presence of BADGE and BFDGE in the manufacture of those materials and articles may only be continued until 31 December 2004 [9, 10]. These limits are full harmonised with already known European Community Commission Directives (90/128/EEC, 1999/91/EC, 2001/61/EC, 2001/62/EC, 2002/16/EC, 2002/17/EC, 2002/72/EC).

In this paper, an evaluation of significance of bisphenols degradation in used food simulants during can lacquers testing is reported.

**EXPERIMENTAL**

**Chemicals.** The following standard compounds from Fluka, Switzerland were used: bisphenol A diglycidyl ether (BADGE, 97%), bisphenol A-bis-(2,3-dihydroxypropyl)-ether (BADGE.2H₂O, 97%), bisphenol A-(3-chloro-2-hydroxypropyl)-(2,3-dihydroxypropyl)ether (BADGE.H₂O.HCl, 95%), bisphenol A-glycidyl-(3-chloro-2-hydroxypropyl)ether (BADGE.HCl, 95%), bisphenol A-glycidyl-(2,3-dihydroxypropyl)ether (BADGE.H₂O, 95%), bisphenol A-bis-(3-chloro-2-hydroxypropyl)ether (BADGE.2HCl, 99%), bisphenol F diglycidyl ether (BFDGE, 97%, a mixture of 3 isomers: o-o, o-p, p-p), bisphenol F-bis-(2,3-dihydroxypropyl)ether (BFDGE.2H₂O, 95%, a mixture of 3 isomers: o-o, o-p, p-p), bisphenol F-bis-(3-chloro-2-hydroxypropyl)ether (BFDGE.2HCl, 97%, a mixture of 3 isomers: o-o, o-p, p-p). Bisphenol A (BPA, 99%) and bisphenol F (BPF, 98%) were obtained from Sigma, Germany.

**Reagents.** Acetonitrile (99%) was purchased from Fluka, Switzerland. The 99% acetic acid was obtained from Penta, Czech Republic, 10% and 95% ethanol were obtained from Lachema, Czech Republic.

**Experimental.** Standard stock solutions in acetonitrile were prepared of all the compounds investigated separately at concentration level 1 mg/ml, these solutions were first subdivided to concentration 50 μg/ml. A standard stock mixture solution was prepared from all standard stock solutions of each bisphenol (500 μl of each standard stock solutions were added to 4500 μl of acetonitrile). The solutions of BPA, BADGE and BFDGE in four simulants (distilled water, 10% ethanol, 95% ethanol and 3% acetic acid) were prepared in concentration 3 μg/ml of each compound from standard stock solutions (60 μl of standard stock solution were added to 940 μl of food simulant). Mixture solutions of all bisphenols were prepared in concentration 3 μg/ml of each food simulant (60 μl of standard stock mixture solution were added to 940 μl of food simulant).

The stability of BPA, BADGE and BFDGE in acetonitrile and in food simulants and creation of their derivatives were tested by means of samples measurements with four-hour interval during 48 h. Mixture solutions of bisphenols in food simulants were analysed at the same conditions. All stability tests were carried out at the temperature of 23°C.

**Instrumentation.** The HPLC system consisted of a high pressure gradient pump (P580, Gynkotek,
RESULTS AND DISCUSSION

After 48 hours BPA, BADGE and BFDGE were least stable in 3% acetic acid (79%, 33% and 25%, respectively) and most stable in 95% ethanol (85%, 96% and 8%, respectively).

In the mixture of all bisphenols (initial concentration 3 µg/ml of food simulants) these trends of increase or decrease of each compounds were observed (Figure 2): BADGE and BFDGE amounts decreased at most in 3% acetic acid, at least in 95% ethanol; BPA and BPF amounts increased at most (due to decomposition of the other derivatives to BPA and BPF) in 3% acetic acid, at least in 95% ethanol; BPA and BPF amounts were increased at most (decomposition of the other derivatives to BPA and BPF) in 3% acetic acid, at least in 95% ethanol; BADGE.2HCl and BFDGE.2HCl were produced at most in distilled water; BADGE.2H₂O and BADGE. HCl amounts were highest in distilled water and 10% ethanol; the highest amounts of BFDGE.2H₂O, BADGE. H₂O.HCl and BADGE. H₂O in 3% acetic acid were observed.

In simulants containing only BADGE (3 µg/ml) at the beginning, BADGE was broken down fast-
est in 3% acetic acid (Figure 3), BADGE.2H2O was progressed only in 3% acetic acid, the other compounds (BPA, BADGE.H2O.HCl and BADGE.H2O) were created at most in 3% acetic acid, too. This food simulant seemed as critical for BADGE and production of its derivatives.

The last experiment (Figure 4) was aimed to monitoring of BFDGE derivatives presence from BFDGE solution in food simulants (initial concentration was 3 µg/ml). BFDGE was broken down most in 3% acetic acid, BPF was created at most in 10% ethanol, at least in 95% ethanol, and BFDGE.2H2O amount was highest in 10% ethanol whereas in 95% ethanol did not create at all. For BFDGE decomposition are most sensitive food simulants 10% ethanol and 3% acetic acid.

CONCLUSIONS

Because the package stability is indirectly tested by means of food simulants, it is necessary to verify stability of bisphenols under conditions of migration testing to avoid false positive/negative results caused by their possible decomposition in used simulant. Time progress of each bisphenol derivative presence was in each food simulant different, it can not be predicted. Generally, we can say the most sensitive food simulants relative to risk of decomposition and creation of derivatives were 3% acetic acid and 10% ethanol. Contrariwise 95% ethanol was the most neutral for derivatives formation.

References