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Food Additives and Contaminants



The occurrence of extractible ink residuals in packaging materials used in the Czech Republic.

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Abstract

Residues of printing ink components were determined in 94 samples of packaging materials commercially used in the Czech Republic for food packaging. The samples which were tested included printed polyethylene and polypropylene films, co-extruded and laminated films, paperboard beverages boxes, foils for thermo sealing of polystyrene cups and polypropylene cups. Printing ink components were extracted with diethylether, then separated and determined using GC/MS. Fifty compounds potentially originating from printing were isolated, identified and quantified. No acute health risk for consumers were identified even though several findings of high levels of photoinitiators (e.g. in PET films for thermo sealing of polystyrene cups) as well as plasticizers (acetyl tributyl citrate, tributyl aconitate, 2-butoxyethyl oleate and 2-ethylhexyl diphenyl phosphate in co-extruded films) indicate that their real migration into food and or food simulants needs to be undertaken for a proper safety evaluation.

Keywords: food packaging, printing inks, migration, food safety

Introduction

Printing inks used in food packaging production contain many substances that have not been toxicologically evaluated, since they are not coming into direct contact with food. However, these substances (e.g. pigments, plasticisers, solvents, photoinitiators, stabilizers, their breakdown products, etc.) may be transferred from the printing to the food contact surface either by penetration through the packaging material or via the set-off transfer phenomenon (transport of printing ink constituents from printed surface to the unprinted side of another sheet in a stack or roll).

When the printing ink components reach the food contact layer of the package, they could migrate into the packaged food due to extraction by food, evaporation and/or steam distillation during storage and/or heating in original package (Sun Chemical 2007). As printing is not in a direct contact with food no specific legislation concerning printing inks for food packaging has been agreed so far in EU. The Framework Regulation (EC 2004)

applicable to all food packages only states that printing for food packages in EU will be in future controlled by particular system of directives and regulations. At present materials and articles intended to come in contact with foods should comply with the general criteria laid down in Art. 3 of above mentioned Framework Regulation, i.e. should not transfer their constituents in food in quantities, which could endanger the human health or bring about unacceptable changes in composition or characteristics of foodstuffs. These criteria are also reiterated in the Council of Europe Resolution (Council of Europe 2005). To prove the conformity with above mentioned demand the risk assessment is necessary. This is the responsibility of packaging material and/or food contact article producer. The Framework Regulation (EC 2004) also requires the traceability of food contact materials and articles at all stages as well as production by Good Manufacturing Practice (EC 2006, EuPIA 2008, Sun Chemical 2007).

The influence of the printing system on food packaging safety, mainly migration of solvents, plasticizers and photoinitiators, has been already studied. Skjevrak et al (2005) tested migration from 75 samples of plastic laminates for food packaging into oil and/or distilled water and they found eight major migrants with level of migration above 0.3 mg/kg, six of them originated (or could have originated) from printing and/or coating, i.e. dioctyl adipate, diisooctyl adipate, 2-(2-butoxyethoxy)ethanol, bisphenol A diglycidyl ether (BADGE), methyl ester of dehydroabietic acid and N-ethyl-toluenesulfonamide. They also identified four primary aromatic amines originated from printing (2-methyl-aniline, 2,4,-dimethylaniline, 2-methoxyaniline and 4,4'-methylene-dianiline) at migration level <0.02 mg/kg. Nevertheless their results showed that migration of non-authorized substances in found level did not present a risk to consumer health. Migration of plasticizers (mainly esters of phthalic acid, adipic acid, sebacic acid, citric acid and mellitic acid, but also N-methyl- and N-ethyl-toluensulfonamide) from printing inks into packaged foodstuffs was also reported (Nerin et al. 1993, Balafas et al. 1999, Piergiovanni et al. 1999).

The danger of residues of photoinitiators (PI) migrating from UV-cured printing of food packages has been reported (Castle 1997). Their transfer by set-off caused significant damage for producers of beverages like milk, cocoa or juice packaged in paperboard packages in 2005, when the substances 2-isopropyl thioxanthone (ITX) and 2-ethylhexyl-4-

dimethylaminobenzoate (EHDAB) were detected in packaged products at levels up to 300 μ g/kg food. (EFSA 2005, EuPIA 2005b) These findings often exceeded a maximum migration level of 50 μ g/kg food, which was announced by the European Food Safety Authority (EFSA) as an acceptable threshold for substances with no genotoxic potential (EFSA 2005, Gil-Vergara et al. 2007, Benetti et al. 2008). Kleinschnitz and Schreier (1998) reported the determination of 2,4,7,9-tetramethyl-5-decyne-4,7-diol in mineral water packaged in paperboard beverage boxes up to levels of 50 μ g/l. The origin of this substance was a surfactant in water-based printing inks. Aurela et al. (2001) described the identification of alkylbenzenes (alkyl chain C₁₀-C₁₃) in 10 out of 15 samples of offset-printed food packaging made of paperboard. Alkylbenzenes are used as solvent components in some offset printing inks and the authors found migration into packaged product up to 2 mg/kg.

The main aim of this study was to screen polymer printed packaging materials commercially used in Czech Republic to obtain objective data for an evaluation of possible contamination of packaged food with printing ink constituents.

Materials and methods

Packaging materials:

Printing ink residuals testing. 94 food packaging materials were tested. All of them are currently used for food packaging in Czech Republic. The set of samples included:

- i. 3 films made of low density polyethylene (LDPE) and 2 samples from polypropylene (PP) with direct printing on outside surface.
- ii. 8 laminates PP-metalized/LDPE, 2 laminated films of metalized polythylene terephthalate (PET) and LDPE (PET-met/LDPE) and one laminate PP/Al/LDPE with reverse printing on inside surface of upper layer.
- iii. 2 laminates PET/LDPE, 9 coextruded films PP/LDPE, 16 films of laminates paper/Al/LDPE and 10 laminates paper/LDPE with printing on the outside surface.
- iv. 15 laminates paper/Al/LDPE for production of beverages boxes with printing on outside paper surface.
- v. 8 aluminium foils and 15 PET films coated with thermosealable lacquer for sealing polystyrene (PS) cups with printing on the outside surface.
- vi. 2 cups of PP printed on the outside surface.

Concerning printing techniques used for tested packaging materials production 53 samples and 26 packaging materials were printed with flexography using UV-cured and not UV cured inks, respectively. 15 samples were produced using gravure print.

Analytical methods:

Determination of free printing ink constituents by diethyl ether extraction. 1 dm² of tested packaging material was extracted with 50 ml of diethyl ether (p.a., Sigma-Aldrich Chemie,GmbH) in SoxtecTM 2043 extractor (Foss Analytical, DK) for two hours. Diethyl ether extract was evaporated to dryness at 40 °C using a vacuum evaporator and redissolved in 2 ml of diethyl ether. 1 µl of this solution was injected into a gas chromatograph coupled with a mass spectrometry detector and analysed at following conditions: gas chromatograph -Agilent 6890N (Agilent Technologies); detector – Agilent 5973N mass detector, electron impact ionisation 70 eV, temperature 280 °C; capillary column - DB-5 (30 m x 0.25 mm x 0.25 µm); mobile phase - He, flow rate 0.6 ml/min, linear speed 28.9 cm/s; injection - 1 µl using split 1 : 100, temperature 300°C; column temperature - 70 °C for 5 minutes, increase 15 °C/min to 300 °C, 300 °C to the analysis end. Identification of separated substances consisted in comparison of obtained mass spectra with the spectrum library of used chromatography software (NIST MS Search 2.0) and its confirmation using the mass spectra of analysed standards. The quantification was done using diethyl phthalate (p.a., standard for GC, Sigma-Aldrich Chemie, GmbH) as the internal standard. At least three parallel samples for each tested packaging film were analysed. The results in the next text are expressed as mean values± standard deviations.

The analytical deviation for reference compounds at 10 mg/l (according with migration level of 10 μ g/dm²) concentration level in diethylether solution typically corresponded to 5-10% RSD and at 100mg/l (100 μ g/dm²) to 3-5% RSD.

Results and discussion

Having planned this study, we had to overpass some problems. Firstly we did not get either interest for cooperation from printing ink producers so that we had to obtain the packaging material samples from food and packaging material producers, i.e. we could not exploit any

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more detailed knowledge on tested printing parameters. Unfortunately there was no possibility to obtain and test unprinted packaging materials as controls. As printing inks form quite complex chemical systems and due to little information on tested printings composition, we decided to analyze the packaging materials samples using the gas chromatography coupled with mass spectroscopy detector as this technique offers the most convenient identification of separated substances. Moreover the potential migrants capable of transfer from printing to packaged food, which could present the threat for consumer, should be first of all organic substances of lower molecular weight with sufficiently low boiling temperature.

Three techniques of isolation of printing ink constituents were originally tested, i.e. adsorption on Tenax TA sorbent, application of solid phase micro extraction method (SPME) and direct extraction with diethyl ether. The last procedure was found the most efficient, as the number of isolated and identified substances was higher comparing with the other techniques. The examples of typical chromatograms are shown in Figure 1

Identification of ink components released from tested films

From the tested films 50 substances (see Table I) were isolated and identified in amount exceeding 0.001 mg/dm². According to the published data, these substances could originate from printing inks even it is obvious that extraction with diethyl ether did not enable to distinguish between additives released from polymers and those really extracted from printing as only the printed packaging materials were tested. Extractible levels of identified substances ranged from 0.0015 \pm 0.0002 mg/dm² for lauramide to 0.898 \pm 0.017 mg/dm² for acetyl tributyl citrate.

The presence of substances obviously originated from printing, which are not allowed for polymer food contact materials, is interesting, e.g. dichlor benzenamine (probably the breakdown product of aryl pigments), six photoinitiators and/or their breakdown derivatives (isopropyl thioxantone, 4-phenyl benzophenone, 4-hydroxy benzophenone, ethyl-4-dimethyl aminobenzoate, 2-ethylhexyl-4-dimethylaminobenzoate and trimethyl benzaldehyde). On the other hand there were substances present in amount exceeding 0.500 mg/dm², e.g. diethylhexyl adipate (up to 0.698 ± 0.014 mg/dm²), 2-ethylhexyl diphenyl phosphate (0.873 ± 0.026 mg/dm²) and acetyl tributyl citrate (0.898 ± 0.017 mg/dm²).

The most frequent substance found in tested samples of packaging materials was diethylhexyl adipate, which was identified in 24 samples included beverage board boxes, laminated and co-extruded packaging films and polyethylene terephthalate films for sealing of cups with yoghourt. The maximum content $0.698 \pm 0.014 \text{ mg/dm}^2$ was found in beverage board box printed using flexography. In 23 samples (paper board boxes, laminated and/or co-extruded films) oleamide was identified in maximal level of $0.220 \pm 0.004 \text{ mg/dm}^2$. The highest concentration of printing ink constituent (i.e. $0.898 \pm 0.017 \text{ mg/dm}^2$) was found for acetyl tributyl citrate in co-extruded film for biscuit packaging. This substance was identified in twelve more packaging films. 2-ethylhexyl diphenyl phosphate was identified in 8 samples of co-extruded and/or laminated films for biscuit packaging at maximum level of $0.873 \pm 0.026 \text{ mg/dm}^2$. Erucamide was found in one sample of beverage board box at level $0.232 \pm 0.007 \text{ mg/dm}^2$.

Seven PIs were identified in samples printed with UV curable inks. Ethyl 4dimethylaminobenzoate was the identified in ten samples of PET films for sealing of polystyrene cups at maximal level of $0.151 \pm 0.005 \text{ mg/dm}^2$, 4-phenyl benzophenone was found in 9 samples including laminated films for packaging of spices, soup condiment and/or dehydrated soups as well as PET films and aluminium foils for sealing polystyrene cups at maximal level $0.139 \pm 0.006 \text{ mg/dm}^2$. The more known PIs 2-isopropyl thioxanthone (ITX) and 2-ethylhexyl 4-dimethylaminobenzoate (EHDAB) were found only in 4 and 2 cases, respectively. This fact is probably the consequence of the attitude of food producers in Czech Republic, whose generally refuse packaging materials printed with inks containing ITX and EHDAB. The highest found contents of ITX and EHDAB were $0.182 \pm 0.010 \text{ mg/dm}^2$ and $0.0759 \pm 0.0023 \text{ mg/dm}^2$, respectively.

Tributyl aconitate was identified in 14 samples of packaging materials (beverage boxes, laminated films) at level up to $0.0764 \pm 0.0046 \text{ mg/dm}^2$, toluene-2,4-diisocyanate in 12 samples (PET and aluminium sealing foils, co-extruded and laminated films) up to $0.0611 \pm 0.0048 \text{ mg/dm}^2$, dibutyl sebacate in two films for biscuit and spice packaging up to $0.0616 \pm 0.0043 \text{ mg/dm}^2$ and 2-butoxy ethyl oleate in one laminated film for vanilla sugar packaging at level $0.0616 \pm 0.0037 \text{ mg/dm}^2$.

 authors.

The above mentioned results are generally comparable with findings of Skjevrak et al. (2005) for laminated food packaging films. The main difference is an absence of N-ethyl-toluene sulfonamide (NETSA). NETSA was used as plasticizer in resins, cellulose acetate, nitrocellulose, lacquers adhesives and inks and in Norwegian study this substance was isolated from printed laminated films in by far the highest amount. Its absence in materials tested in this study should certify the intent of packaging film producers not to use NETSA in printing inks (Skjevrak et al. 2005). Besides the above mentioned residues, fifteen substances were detected but not identified, and so far were characterised only by mass spectra, but were present at quite significant levels (about 50-100 µg/dm²), too. Their identification will pose one of the main tasks for the

Evaluation of possible risk of potential migrants originated from printing inks

When migration of substances not included in the EU positive list of monomers and/or additives for food contact polymer is identified, assessments of health risks are usually carried out. In this study the content of substances which could be released and potentially transferred into packaged product was determined, but no data on real migration were obtained. It means that no proper health risk assessment could be done. Nevertheless the possible danger due to presence of identified substances could be estimated.

From substances not included in the EU positive list identified in Table 1 the occurrence of four PIs (ethyl 4-dimethylaminobenzoate, EHDAB, 4-phenyl-benzophenone and ITX) at levels up to 0.182 mg/dm² could pose problems. These substances were identified in the printing of barrier films for spice, condiment and or dehydrated soups packaging. These materials eliminate the possibility of PIs penetration through the package. Considering the extent of set-off transfer in agreement with this study results, i.e. 1 % of PI amount in lacquer per month at 40 °C, we can expect the safety of packaging material for approximately 2 year storage at 20 °C. Similar situation can be expected for aluminium foils for thermo sealing of polystyrene cups with yoghourt, moreover there is advantage in smaller area of foil in contact with food. In the PET films for thermo sealing of polystyrene cups the maximal found amount of PI reached the level 0.151 mg of ethyl 4-dimethylaminobenzoate per dm². Due to good

barrier parameters of PET film and the layer of thermo sealable lacquer on the base of polyvinyl dichloride (PVdC) as well as the fact that the area of such packaging material in the contact with food is quite limited the real risk for consumer could be considered as quite low. Nevertheless the migration tests of these materials would be advisable.

Acetyl tributyl citrate was identified in different types of packaging materials including coextruded PP/LDPE films in levels up to 0.898 mg/dm². Due to the absence of efficient barrier it would be suitable to verify migration of this additive through the tested packaging films even if acetyl tributyl citrate is accounted the material of low toxicity. Similar situation could be stated for tributyl aconitate, which was found in 14 tested samples in maximal level 0.0764 mg/dm², and 2-butoxyethyl oleate that was identified only in one tested sample in amount 0.0616 ± 0.0037 mg/dm².

Considering identified substances included in EU positive list the high content of 2-ethylhexyl diphenyl phosphate in five tested samples of co-extruded films (up to 0.873 mg/dm²) is suspicious. The set specific migration limit for this additive is 2.4 mg/kg, i.e. 0.4 mg/dm², and in agreement with the results obtained by this study it could be surpassed in contact with food simulants. In this case also the migration test of relevant packaging materials should be done for final assessment.

The migration tests of PIs, acetyl tributyl citrate, tributyl aconitate, 2-butoxyethyl oleate and 2-ethylhexyl diphenyl phosphate from tested packaging materials samples will be carried out in the next part of project solution.

Conclusion

The main results of carried out experiments can be summed as follows:

- The determination of residues of printing inks in 94 food packaging materials commercially used in Czech Republic did not indicate any acute health risk for food consumer.
- ii) Suspicious findings of higher levels of PIs in PET films for thermosealing of polystyrene cups as well as acetyl tributyl citrate, tributyl aconitate, 2-butoxyethyl

 oleate and 2-ethylhexyl diphenyl phosphate should be completed with information on real migration into food and or food simulants.

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References

Ash M and Ash I. 1999. Handbook of Food Packaging Chemicals and Materials. ISBN 1-890595-11-X, Endicott U.S.A.: Synapse Information Resources, Inc.

Aurela B, Ohra-aho T, Söderhjelm L. 2001. Migration of alkylbenzenes from packaging into food and Tenax[®]. Packaging Technology and Science, 14(2): 71-77.

Az R, Dewald B, Schnaitmann D. 1991. Pigment Decomposition in Polymers in Applications at elevated Temperatures, 15, 1-14.

Balafas D, Shaw KJ, Whitfield FB. 1999. Phthalate and adipate esters in Australian packaging materials. Food Chemistry, 65(3): 279-287.

Benetti C, Angeletti R, Binato G, Biancardi A, Biancotto G. 2008. A packaging contaminant: isopropyl thioxantone (ITX) in dairy products. Analytica Chimica Acta, 617: 132-138.

Castle L, Mayo A, Gilbert J. 1989. Migration of plasticizers from printing inks into food. Food Additives and Contaminants, 6: 437-443.

Castle L, Damant AP, Honeybone CA, Johns SM, Jickells SM, Sharman M, Gilbert J. 1997. Migration studies from paper and board food packaging materials. II. Szrvey for residues of dialkylamino benzophenone UV-cure ink photoiniciators. Food Additives and Contaminants, 14(1): 45-52.

CEPE 2007. Lists of monomers and additives. CEPE web site

(www.cepe.org/EPUB/easnet.dll/GetDoc?APPL=1&DAT_IM=02091C&TYPE=PDF, 5.1.2009)

Cole Palmer 2005. 2,4-di-tert,-butylphenol MSDS. Cole Palmer web site. (http://www.coleparmer.com/Catalog/Msds/27061.htm, 31.12.2008)

Council of Europe 2005. Council of Europe Resolution ResAP (2005)2 of 14th September 2005 on packaging inks applied to the non-food contact of food packaging materials and articles intended to come into contact with foodstuffs.

Science Lab 2008. Dioctyl adipade MSDS. Science Lab.com web site. (www.sciencelab.com/xMSDS-Dioctyl_Adipate-9923845, 31.12.2008)

Dow Chemical Company. 2008. Glycol ethers for intermediates. Product Information, FormNo.110-00756-0304.

(www.dow.com/webapps/include/getdoc.aspx?objectid=&filepath=oxysolvents/pdfs/noreg/11 0-00756.pdf&pdf=true, 31.12.2008)

EC 2002. Commission Directive 2002/72/EC relating to plastic materials and articles intended to come into contact with foodstuffs. The Commission of the European Communities, 6.8.2002.

EC 2004. Regulation (EC) No 1935/2004 on materials and articles intended to come into contact with food and repealing Directives 80/590/EEC and 89/109/EEC. The European Parliament and the Council of the European Union, 2004.

EC 2006. Commission Regulation (EC) No 2023/2006 on good manufacture practice for materials and articles intended to come into contact with food. The Commission of the European Communities, 22.12.2006.

EFSA 2005. Opinion of the scientific panel on food additives, flavourings, processing aids and materials in contact with food on a request from the Commission related to 2-isopropyl thioxanthone (ITX) and 2-ethylhexyl-4-dimethylaminobenoate (EHDAB) in food contactmaterials. The EFSA Journal, 293: 1-15.

EFSA 2007. Scientific Opinion of the Panel on food additives, flavourings, processing aids and materials in contact with food (AFC) on a request related to a 14th list os substances for food contact materials Question N° EFSA-Q-2006-1, EFSA-Q-2006-178, EFSA-Q-2006-116. The EFSA Journal, 452 to 454: 1-10.

EFSA 2008. Scientific Opinion of the Panel on food contact materials, enzymes, flavourings and processing aids (CEF) on 21st list of substance for food contact materials. The EFSA Journal (2008), 888-890, 1-14.

EuPIA 2005. Opinion on isopropyl thioxantone (ITX) in food packaging inks. December 2005.

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EuPIA 2008. Guideline on Printing Inks applied on the non-food contact surface of foodpackagematerialsandarticles,April2008.(http://www.contactalimentaire.com/index.php?id=520&task=show&uid=387&target=4&category=&cHash=4f77ee6b6a, 5.1.2009)

FedChem 2002. Manalox 230 (OAO) MSDS. FedChem, LLC web site. (www.fedchemproducts.com/languages/fedchem-

brittish/pdfs/manalox/MANALOX_230_AOA.PDF, 5.1.2009)

Fischer Scientific 2005. 4-Hydroxybenzophenone MSDS. Fischer Scientific website. (https://fscimage.fishersci.com/msds/04664.htm , 5.1.2009)

Gil N, Saska M, Negulscu I. 2006. Evaluation of the effects of biobased plasticizers on the thermal and mechanical properties of poly(vinyl chloride). Journal of Applied Polymer Science 102(2), 1366-1373.

Gil-Vergara A, Blasco C, Pico Y. 2007. Determination of 2-isopropyl thioxantone and 2ethylhexyl-4-dimethylaminobenzoate in milk: comparison of gas and liquid chromatography with mass spectrometry. Analytical and Bioanalytical Chemistry 389(2): 605-617.

Good Scents Company 2009. Butyl palmitate. The Good Scents Company web site. (http://www.thegoodscentscompany.com/data/rw1413791.html, 5.1.2009)

ISP 2008. Escalol[®] 507 MSDS. International Specialty Products web site.

(http://online1.ispcorp.com/MSDS/ESCALOL%20507_EN_I.pdf, 31.12.2008)

Kleinschnitz M, Schreier P. 1998. Identification and semi-quantitative determination of a migration contaminant from beverage carton packages into mineral water by on-line solid phase extraction gas chromatography-mass spectrometry (SPE-GC-MS). Chromatographia, 48(7/8): 581-583.

Magnaflux 2007. Zyglo[®] Penetrant ZL-37 MSDS. Magnaflux web site.

(http://www.magnaflux.com/files/library/msds/liquid_penetrant/Zyglo~reg_Penetrant_ZL-37.pdf, 6.1.2009)

MC-Bauchemie 2008. MC-Inject 2700 (Komponente B) MSDS, MC-Bauchemie web site (in Czech). (<u>http://www.mc-bauchemie.cz/download.aspx?file=/datasheets/safety/1178 - MC-Injekt_2700 (Komponente_B)_(CZ).pdf</u>, 31.12.2008)

Nerin C, Cacho J, Gancedo P. 1993. Plasticizers from printing inks in a selection of food packaging and their migration to food. Food Additives and Contaminants, 10(4): 453-460.

Papilloud S, Baudraz D. 2002. Analysis of food packaging UV inks for chemicals with potential to migrate into food simulants. Food Additives and Contaminants, 16(8): 353-359.

Piergiovanni L, Fava P, Schiraldi A. 1999. Study of diffusion through LDPE film of di-nbutyl phthalate. Food Additives and Contaminants, 19(2): 168-175.

PTCL Safety lab 2003a. Safety data for erucamide. Physical and Theoretical Chemistry Lab at Oxford University, web site. (http://msds.chem.ox.ac.uk/ER/erucamide.html, 31.12.2008)

PTCL Safety lab 2003b. Safety data for squalane. Physical and Theoretical Chemistry Lab at Oxford University, web site. (<u>http://msds.chem.ox.ac.uk/SQ/squalane.html</u>, 31.12.2008)

PTCL Safety lab 2007. Safety data for cetyl alkohol. Physical and Theoretical Chemistry Lab at Oxford University, web site. (<u>http://msds.chem.ox.ac.uk/CE/cetyl_alcohol.html</u>, 5.1.2009)

Skjevrak I, Due A, Gjerstad KO, Herikstad H. 2003. Volatile organic components migraing from plastic pipes (HDPE, PEX and PVC) into drinking water. Water Research, 37:1912-1920.

Skjevrak I, Brede C, Steffensen I-L, Mikalsen A, Alexander J, Fjeldal P, Herikstad H. 2005. Non-targeted multi-component analytical surveillance of plastic food contact materials: Identification of substances not included in EU positive list and their risk assessment. Food Additives and Contaminants, 22(10): 1012-1022.

Sun Chemical 2007. Printing for packaging - Low migration printing. Best Practice Guide, revised version 2, December 2007. Sun Chemical Ltd., St Mary Cray, Orpington, United Kingdom.

TCI Europe 2009. Photopolymerization Initiators. TCI Europe web site.

(http://www.tcieurope.eu/en/product/materials-chem/F013.shtml, 6.1.2009)

TradeWinds 2007. TriForceTM Canine Squeeze On MSDS. TradeWinds web site.

(http://www.ginnyweaver.com/duff/triforce/website/download/CanineMSDS.pdf, 6.1.2009)

Wikipedia 2009. E numer. Wikipedia, the free encyklopedia. (<u>http://en.wikipedia.org/wiki/E_number#E1000.E2.80.93E1999_.28additional_chemicals.29</u>, 5.1.2009)

No.	Printing ink residue	CAS- no	Toxicological data	highest content - (mg/dm ² -)	number of occurance-	origin/function	Included in EU positive list for polymers (4, 24)	^	Deleted: Migrant Deleted: µ
1	Acetyl tributyl citrate (1,2,3-Tributyl 2-acetyloxypropane- 1,2,3-tricarboxylate)	77-90- 7	 LD50 intraperitoneal, mouse: >4g/kg; low toxicity by ingestion, skin contact, and intraperitoneal routes; TSCA listed (1) 	<u>0.898±0.</u> <u>017</u>	13	Solvent, film-former and plasticizer for inks, adhesives, coatings (1)	PL		Deleted: .3
2	Butyl hydroxyl toluene (4-methyl-2,6- ditert-butyl-phenol)	128- 37-0	• ADI 0.05 mg/kg bw/d (5)	<u>0.020±0.</u> 002	7	-Antioxidant	$\frac{\text{SML} = 0.5 \text{ mg/dm}^2}{(\text{SCF-L 1})}$		Deleted: .0 Deleted: 3.0
3	Butyl palmitate (butyl hexadecanoate)	111- 06-8	 Maximised Survey- derived Daily Intakes (MSDI- EU) : 0.79 µg/capita/day; modified Theoretical Added Maximum Daily Intake (mTAMDI) : 3500 µg/person/day; Threshold of concern : 1800 µg/person/day (2) 	0.0045±0 .0005	1	-Eubricant (1)	PL (SCF-L 3)		Deleted: kg Formatted: Superscript Deleted: .
4	2-Butoxyethyl oleate (2-butoxyethyl cis-octadec-9-enoate)	109- 39-7		<u>0.0616±0</u> .0037	1	Plasticizer, lubricant (3)			Deleted: .

5	Caprolactam (<i>a</i> zepan-2-one)	105- 60-2	• ADI 0.25 mg/kg bw/d (24)	0.0265±0 .0008	1	Monomer, component of-external colour printing (1,5)	PL, SML(T) = $\frac{2.5 \text{ mg/dm}^2}{(\text{SCF-L } 2)}$	Deleted: . Deleted: 15
6	Dibutyl sebacate (dibutyl decanedioate)	109- 43-3	 LD50 oral, rat 16 g/kg; Mildly toxic by ingestion, experimental reproductive effects; TSCA listed (1) 	<u>0.0616±0</u> .0043	2	Plasticizer, solvent (1)	PL (SCF-L 3)	Formatted: Superscript Deleted: .
7	2,5-Dichloroaniline	95-82- 9	P	<u>0.0031±0</u> <u>.0004</u>		Azo dyes -decomposition product (6)	(limit for primary aromatic amines SML(T) = 0,0016 mg/dm ²)	Deleted: .
8	Diethylhexyl adipate (bis(2-ethylhexyl) hexanedioate)	103- 23-1	• ADI 0.3 mg/kg bw/d (24)	<u>0.698±0.</u>	24	Plasticizer, solvent (1)	PL SML = 3-mg/dm^2 (SCF-L 2)	Deleted: .2 Deleted: 18 Deleted: kg
9	Diisobutyl phthalate (bis(2-methylpropyl) benzene-1,2- dicarboxylate)	84-69- 5	 LD50 oral,rat: 15g/kg, skin,guinea pig: 10g/kg, Mildly toxic by ingestion and skin contact; Experimental teratogen; Reproductive effects; TSCA listed (1) 	<u>0.0152±0</u> .0012	2	Plasticizer, solvent for paints; vehicles for pigment dispersions (1,7,8)	· (SCF-L-6B)	Formatted: Superscript
10	Diisooctyl phthalate (bis(6-methylheptyl) benzene-1,2- dicarboxylate)	27554- 26-3	• ADI 0.15 mg/kg bw/d (24)	<u>0.0048±0</u> .0003	13	Plasticizer, solvent (1,7,8)	PL SML(T) = $1.5mg/dm^2$ (in combination with higher molecular weight esters for DIOP maximally $0.5 mg/dm^2$)	Deleted: 9 Deleted: kg Formatted: Superscript Deleted: . Deleted: 3 Deleted: kg Formatted: Superscript

11	Dioctyl adipate (dioctyl hexanedioate)	123- 79-5	• LD50 oral,rat: 9.1 g/kg, oral, mouse: 15g/kg (9)	<u>0.0053±0</u> .0005	4	Plasticizer, solvent and raw material for adhesives and coatings (1)	(SCF-L-6B)		Deleted:
12	4,4'-Diphenylmethane diisocyanate (1-isocyanato-4-[(4- isocyanatophenyl)methyl]benzene)	101- 68-8	 LD50 oral, rat: > 10 g/kg; LC50 Inhalation, rat: 450 mg/l/4 h (10) 	<u>0.0057±0</u> .0004	2	Polyuretane inks and adhesives (1)	PL QM(T) = 1 mg/kg (as NCO) (SCF-L 4A)		Deleted: .
13	2,4-Di <i>tert</i> -butylphenol	96-76- 4	• LD50 oral, mouse: 700 mg/kg; oral, rat: 2400 mg/kg; skin, rabbit: 2200 mg/kg (11)	<u>0.0071±0</u> .0005	1	UV absorber or degradation product from antioxidants (e.g. Irgafos) (1,12)			Deleted: .
14	Docosan-1-ol	661- 19-8	Low toxicity;TSCA listed (1)	<u>0.0057±0</u> .0005	1	Lubricant, surfactant, plasticizer, solvent (1)	PL (<i>PM/REF No.</i> 33120) (SCF-L 3)		Deleted:
15	Erucamide (cis-docos-13-enamide)	93050- 58-9	Skin, eye and respiratory irritant (13)	<u>0.232±0.</u> 007	1	Slip agent, lubricant(1)	PL (SCF-L 3)		Deleted: 1.5
16	Ethyl 4-dimethylaminobenzoate	97003- 31-1		<u>0.151_10.</u> 005	10	UV absorber, photoiniciator (1.14)			Deleted: .1
17	3-Ethyl-5-(2-ethylbutyl)-octadecane			Approx. 5.0	3				
18	2-Ethylhexyl 4- dimethylaminobenzoate	21245- 02-3	No teratogenic effects;NOEL 40 mg/kg (15)	<u>0.0759±0</u> .0023	2	UV absorber, photoiniciator (1,14)			Deleted:
19	2-ethylhexyl diphenyl phosphate (3-(diphenoxyphosphoryloxymethyl) heptane)	1241- 94-7	• ADI 0.04 mg/kg bw/d (24)	<u>0.873±0.</u> <u>026</u>		Rubber accelerator, -plasticizer, lubricant, - fire retardant (1)	PL SML = 0.6 mg/dm^2 - (SCF-L 2)		Deleted: .4 Deleted: 2.4
20	Glycerol-1-oleate (2,3-dihydroxypropyl cis-octadec-9- enoate)	25496- 72-4		<u>0.0074±0</u> <u>.0006</u>	2	-Lubricant, solvent (1)-	SCF-L 1	·\`````````````````````````````````	Deleted: kg Formatted: Superscript Deleted: .

21	Glyceryl diacetate ((2-Acetyloxy-3-hydroxy-propyl) acetáte)	25395- 31-7	 LD50 oral, mouse: 8.5 g/kg; subcut, rat: 4 g/kg; TSCA listed (1) Low toxicity, official food additive E1517 (16); 	<u>0.0031±0</u> .0002	1	Plasticizer, solvent (1)	PL, SCF-L 1	 Deleted: .
22	Hexadecan-1-ol	8032- 89-1	 LD50 oral, rat: 6.4 g/kg (1) Skin, eye and respiratory irritant (1,17) 	0.0037±0 .0002	2	Dispersion stabilizer, solvent (1)	PL (<i>PM/REF No.</i> - 33120) (SCF-L 3)	 Deleted: .
23	4-hydroxybenzophenone (phenyl-(4-hydroxyphenyl)- methanole)	1137- 42-4	• LD50 oral, mouse: 3724 g/kg; oral, rat: 12086 mg/kg (18)	<u>0.00</u> 64 <u>±0</u> .0004	3	UV stabilizer, photoiniciator (14)		 Deleted: .
24	Isobutyl stearate (isobutyl octadecanoate)	646- 13-9	Primary skin irritant,TSCA listed (1)	<u>0.0393±0</u> .0035	1	Additive into inks, dyes (1)	· (SCF-L-7)	 Deleted: .
25	Isodecyl diphenyl phosphate (1-diphenoxyphosphoryloxy-8- methyl-nonane)	59800- 46-3	 LD50 oral/rat: 15.8 g/kg; LC 50: 96 hr/bluegill: 6.7 g/l (19, 20) 	<u>0.0038±0</u> .0004	1	Plasticizer, lubricant, fire retardant (19)		 Deleted: .
26	Isopropyl 9,10-epoxyoleate (propan-2-yl 8-(3-octyloxiran-2- yl)octanoate)	95007- 80-0		Approx. 4.0	2	Component of light aged varnishes ?		
27	Isopropyl-2-ethylhexanoate (propan-2-yl 2-ethylhexanoate)	67024- 46-8		<u>0.00</u> 23 <u>±0</u> .0002		Plasticizer, solvent, ink gallant (21)		 Deleted:
28	Isopropylthioxanthone (2-Propan-2-ylthioxanthen-9-one)	5495- 84-1		<u>0.182±0.</u> <u>010</u>	4	UV absorber, photoiniciator (14)		 Deleted: 1.9
29	Lauramide (dodecanamide)	1120- 16-7		<u>0.0015±0</u> .0002		Polymer additive; -release agent for food- packaging (1)		 Deleted: .
30	Methyl 2-benzoylbenzoate	606- 28-0		<u>0.0143±0</u> .0011	3	-Photoiniciator-(22)		 Deleted: .

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31	Methyl dehydroabietate (methyl (1R,4aS,10aS)-1,4a-dimethyl- 7-propan-2-yl-2,3,4,9,10,10a- hexahydrophenanthrene-1- carboxylate)	1235- 74-1		Approx. 4.0	8	Cellulose derivative, component of varnishes and printing inks (16)	
32	Methyl margarate (methyl heptadecanoate)	1731- 92-6		<u>0.0064±0</u> .0005	2	Intermediate for detergents, emulsifiers, -stabilizers, resins, lubricant, plasticizers, defoamer in food- contact coatings (1)	 Deleted: .
33	Methyl oleate (methyl cis-octadec-9-enoate)	112- 62-9	 low oral toxicity; mildly irritating to skin; TSCA listed (1) 	0.0036±0 .0004	2	Intermediate for detergents, emulsifiers, -stabilizers, resins, lubricant, plasticizers, defoamer in food- contact coatings (1)	 Deleted: .
34	Methyl palmitate (methyl hexadecanoate)	112- 39-0	TSCA listed (1)	<u>0.0073±0</u> .0005		Intermediate for detergents, emulsifiers, -stabilizers, resins, lubricant, plasticizers, defoamer in food- contact coatings (1)	 Deleted: .
35	Methyl stearate (methyl octadecanoate)	112- 61-8	 experimental tumorigen; questionable carcinogen; TSCA listed (1) 	0.0085±0 .0005	2	Intermediate for stearin acid detergents, -emulsifiers, wetting	Deleted: .

36	7-Methyl-cis-tetradecen-1-ol-acetate	130- 99-6	Approx. 3.0	1	
37	Mesitylaldehyde (2,4,6-trimethylbenzaldehyde)	487- 68-3	<u>0.0074±0</u> <u>.0004</u>	Product of 1 photoiniciators	Deleted:
38	Oleamide (cis-octadec-9-enamide) (trans-octadec-9-enamide)	301- 02-0 • TSCA listed, • LD50 (rat): > 10 g/kg (1)	<u>0.220±0.</u> <u>004</u>	19 Slip agent for printing inks; processed plastics, coatings and films (1)	Deleted: .3
39	Palmitamide (<i>hexadecanamide</i>)	629- 54-9	<u>0.0035±0</u> .0003	2	Deleted: .
40	4-Phenyl-benzophenone (phenyl-(4-phenylphenyl)-methanone)	2128- 93-0	<u>0.139±0.</u> <u>006</u>	UV stabilizer, photoiniciator (14)	Deleted: 8.5
41	1-Phenylbutan-2-one	1007- 32-5	Approx. 3.0	2 Solvent	
42	(2-Phenyl-1,3,-dioxolan-4-yl) methyloleate		Approx. 3.0	1	
43	Phthalic acid	88-99- 3 • ADI 1.0 mg/kg bw/d (24)	<u>0.0089±0</u> .0007	Component of dyes, food packaging adhesives (1)	Deleted:
<u>44</u>	<u>Squalene</u> ((6E,10E,14E,18E)-2,6,10,15,19,23- hexamethyltetracosa-2,6,10,14,18,22- hexaene)	$\frac{7683-}{64-9}$ •	0.0070±0 .0008	<u>5</u> <u>Antioxidant (1)</u>	
<u>45</u>	Styrene	 LD50 oral,rat: 5000 mg/kg; intravenous,mouse: 90 mg/kg; intraperitoneal, mouse): 660 mg/kg (1) 	0.0143±0 .0011	Solvent, raw materials for ink production (1)PL (SCF-L 4B)	 Formatted: Bullets and Numbering

<u>46</u> _	Tetraethyleneglycol diacrylate (2-[2-[2-(2-prop-2- - enoyloxyethoxy)ethoxy]ethoxy]ethyl prop-2-enoate)	17831- 71-9 -		Approx.	Component of adhesives, varnishes - and photopolymers (1)	(SCF-L 8)		Deleted: 44	
<u>47</u> _	Toluene-2,4-diisocyanate -(2,4-diisocyanato-1-methyl-benzene)	584- 84-9	 LD50 oral,rat: 5.8 g/kg; inh.,rat,4h: 14 mg/kg; Strong irritant to eyes, skin, and tissue; TSCA listed (1) 	<u>0.0</u> 611 <u>±0</u> <u>-0048</u>	Component of polyuretane foams, -elastomers, coatings, - adhesives, sealants (1)	PL QM(T) = 1 mg/kg (as-NCO)		Deleted: . Deleted: 45	
<u>48</u> _	Tributoxyethyl phosphate (1-[2-[bis(2- -butoxyethoxy)phosphoryloxy]ethoxy]- butane)	78-51-	 LD50 oral,rat: 3.0 g/kg; intravenous,mouse: 180 mg/kg, skin,rabbit >16 ml/kg; TSCA listed (1) 	<u>0.0</u> 344 <u>±0</u> 	Plasticizer for most resins and elastomers; coalescing 1solvent/plasticizer for- acrylic-base polish, gloss paints, adhesives (1)	(SCF-L-6B)		Deleted: . Deleted: 46	
<u>49</u> _	Tributyl aconitate (1,2,3-Tributyl cis-prop-1-ene-1,2,3- tricarboxylate)	7568- 58- 3 -		<u>0.0764±0</u> <u>-0046</u>	14Plasticizer (23)			Deleted: . Deleted: 47	
<u>50</u> _	Triphenyl phosphate - (diphenoxyphosphoryloxybenzene)	115- 18	 LD50 oral, rat: 3.5 g/kg; subcut.,cat: 100 mg/kg; skin,rabbit: >7.9-g/kg; toxic by inhalation, skin contact slow absorption (1) 	<u>0.0</u> 11 <u>9±0</u> <u>-0009</u>	Flame retardant plasticizer for coatings, lacquers; 1	(SCF-L-6B)		Deleted: . Deleted: 48	
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49	Squalene ((6E, 10E, 14E, 18E)-2, 6, 10, 15, 19, 23- hexamethyltetracosa-2, 6, 10, 14, 18, 22- hexaene)	7683- 64-9		7.0	5	Antio
50	Styrene	100- 42-5	LD50 oral,rat: 5000 mg/kg; intravenous,mouse: 90 mg/kg; intraperitoneal, mouse): 660 mg/kg (1)	14.3	1	Solve mate prode



Figure 1. Chromatograms of diethylether extracts from co-extruded polypropylene film with flexography print used for bisquit packaging (A) and laminated paper/Al/LDPE film with UV cured flexography printing used for spice packaging (B) (BHT - buty lhydroxy toluene, IS – internal standard = diethyl phthalate)