INVESTIGATION OF SOLVENT RETENTION IN GRAVURE PRINTED CARDBOARD PACKAGING

ELIZA ANGELI[*] and ROZÁLIA SZENTGYÖRGYVÖLGYI[**]

[*]*Obuda University, Doctoral School on Materials Sciences and Technologies, 6 Doberdo ut 1034, Budapest, Hungary*
[**]*Obuda University, Rejto Sandor Faculty of Light Industry and Environmental Engineering, 6 Doberdo ut 1034, Budapest, Hungary*
✉ *Corresponding author: Rozália Szentgyörgyvölgyi, szentgyorgyvolgyi.rozsa@rkk.uni-obuda.hu*

The presence of residual solvents in gravure printed paper packaging might change the taste and flavour of the packed products. In order to avoid off-flavour and off-taste effect, solvent retention values must be kept under the maximum tolerance and consequently, there is a need to identify fast and aqurate methods to measure solvent retention in gravure printed packaging materials. In this study, the influence of moisture content on solvent retention in gravure printed packaging board was studied by the gas chromatography technique. Folding boxboard (FBB) samples with different moisture content have been printed by rotogravure and then solvent retention was measured at four different time intervals. Ethanol and ethyl acetate, which are considered as critical solvents in gravure printing, were studied for individual and total solvent retention and the results have been compared with the specified tolerances in every time interval. It has been found that the decrease of board moisture content results in a decrease of absorbed solvent simultaneously with an increase of solvent evaporation dynamics. Consequently, moisture content has a notable effect on cellulose based cartonboard solvent retention and has to be considered as a remarkable variable in solvent retention analysis.

Keywords: gravure printing, moisture content, solvent retention, evaporation, gas chromatography

INTRODUCTION

The printed substrate that comes in contact with food is required to be manufactured according to strict food industrial standards mainly due to health reasons; also, its composition must be identified. Gravure printed packaging materials are widely used in the food industry. Due to solvent-based inks, a gravure printed substrate always contains a certain amount of residual solvents, which might have an influence on the sensory properties of the packed product, such as odour, taint and flavour. Human senses of smell and taste are sensitive enough to detect even very small amounts of retained solvents.[1,2] In consequence, it is necessary to measure the solvent retention of packaging materials, and make sure it does not exceed the specified limits. The retained solvent amount has been more and more difficult to keep within tolerance limits since challenging graphics require a high solvent ratio of the gravure printing inks applied and due to the high production speed on rotogravure machines. In a series of investigations, we aim to study the main components and properties of cellulose based FBB cartonboard, which might have an influence on solvent resistance.

Almost all packaging materials contain printings. The printing quality requirements are defined by the package design. Gravure printing is considered the best printing method to achive high quality print results, especially when designs with special metallic colours are requested. In the gravure printing method, the liquid ink is transferred from a metal based cylinder to the surface of the substrate. The metal based image cylinder is rotating in the ink tank, consequently the full surface of the cylinder is covered by ink, which is removed by a doctor blade from the non-image areas. The ink from the image cells is transferred to the substrate surface by high pressure generated by the impression roller (Figure 1). Each colour is printed by one printing unit; after each printing step the ink layer is dried and solvents are evaporated in the drying unit by heating the substrate with hot air.[3]

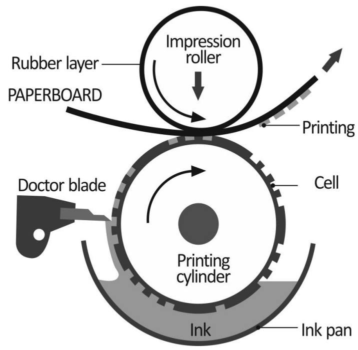

Figure 1: The principle of gravure printing

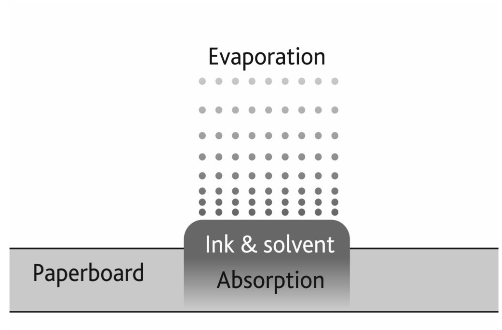

Figure 2: Ink absorption and evaporation drying principle

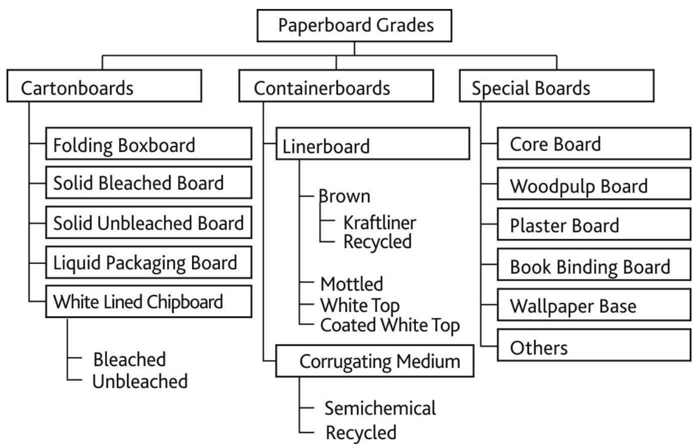

Figure 3: Classification of paperboard grades

After drying, a part of the solvents remains in the ink and is absorbed into the cardboard from the ink layer. This is the solvent retained in the substrate. The liquid gravure printing ink consists of pigments, resins and solvents, it is manufactured and used with low viscosity and with conventional or metal pigments. Volatile solvents are particularly important in the gravure technology, where they are used in order to settle low viscosity and to change pigment concentration and ink density. The main solvents used in the industry are the following: alcohols, esters, aliphatic and aromatic compounds, glycols and ketones.[3,4,5] Figure 2 shows the solvent-based gravure ink absorption and evaporation drying principle; drying is done at high temperature, speed and ventillation.

The ready-made printed package always contains a certain amount of solvents, but the use of metallic inks could effect higher solvent retention as thicker ink film layers are required. Metallic ink components behave like a physical barrier against solvent evaporation. In order to avoid the solvent retention problem, water-based inks should obviously be a reasonable solution, but the print quality and results of water-based inks are not as good as those of solvent-based inks, especially in the case of metallic colours. It is worth noting that the solubilizing amine in water-based inks could be retained in the printed packaging and cause health hazards, while remaining undetectable by the gas-chromatography test.[1,3,4]

Paperboards are classified into three categories: cartonboards, containerboards and special boards, as shown in Figure 3. Paperboard basis weight is usually higher than 150 g/m^2. Cartonboard is a common name for paper products used for packaging cartons, consisting of three or more pulp layers simultaneously manufactured on a multilayer paperboard machine. Cartonboard packaging materials are mainly used for food, cigarettes, milk and pharmaceutical products.[6,7]

Cartonboards are divided into several subgrades. Table 1 shows the typical classification – based mainly on the raw materials used – with abbreviation of the grades used in the paper and board industry. Most of the cartonboard grades are pigment coated for good print results and properties; the top side is often double coated, sometimes triple coated; the back side can be either coated or uncoated according to the printability and design requirements.[6,7]

The FBB cartonboard is widely used in the packaging industry, but typically in cosmetics, tobacco, pharmaceutical, confectionery and food industrial segments in the grammage range of 160-450 g/m^2. The general structure of the FBB multiply cartonboard, from top to back side: coating layer (2 or 3 coating layers); top ply – chemical pulp (bleached softwood or bleached hardwood pulps); middle ply – mechanical pulp (groundwood, pressure groundwood, thermo-mechanical pulp) or CTMP (Chemi-Thermo-Mechanical Pulp) and machine broke added; back ply – chemical pulp (bleached softwood or bleached hardwood pulps). Depending on the end-use requirements, the top side of FFB can be double or triple coated, the back side can be single coated or uncoated.[6] A typical FBB structure can be seen in Figure 4.

Wood fibers are hygroscopic, they absorb water readily and they swell under the influence of water. The paper moisture content is the ratio of water absorbed and divided by total board mass. The moisture content of paper depends on the relative humidity of the air and the equilibrium temperature, when in equilibrium with the surrounding air.[8] Moisture is stored in paper in capillaries and pores in the form of liquid and vapour, as well as in the form of physically bound water between the cellulose fibres, exhibiting potential for hydrogen bonding.[9]

Table 1
Cartonboard grades and abbreviations

Grade	Abbreviation
Folding boxboard	FBB
White lined chipboard	WLC
Solid bleached (sulfate) board	SBS
Solid unbleached (sulfate) board	SUS
Liquid packaging board	LPB

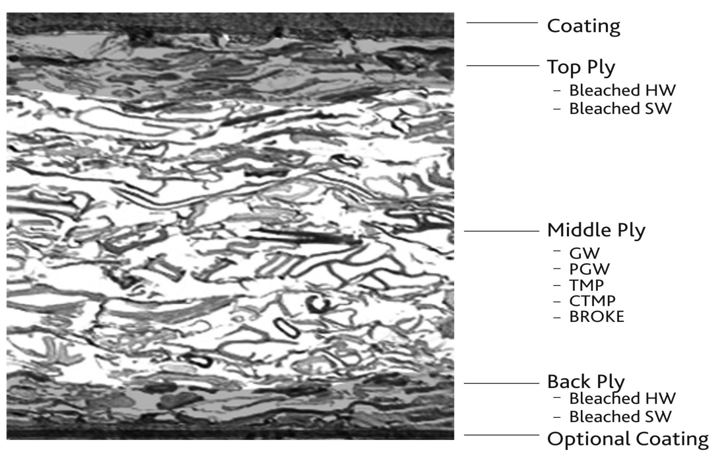

Figure 4: Typical folding boxboard structure

Papermaking fibers absorb water either as free water (interfiber free water in the pores between the fibers, intrafiber free water in the lumen of fibers) or as bound water (freezing bound water (FBW) in the pores of fiber wall, or non-freezing bound water (NBW) that is chemically bonded to the hydroxylic and carboxylic acid groups in fibers).[8] Water in the macropores within the fibre cell wall has similar thermodynamic properties to those of interfiber water and therefore it should also be regarded as bulk water (free water), as Maloney *et al.* observed.[10] Bound water exists in the micropores within the cell wall and it is in a certain state of interaction with pulp. NBW is directly bound water, i.e., the first 1-3 layers of water adjacent to the surface, NBW interactions with pulp prevent the water from freezing. FBW is indirectly bound water, i.e., the water in the micropores not in direct contact with the surface. When the moisture content is lower than 10%, only NBW exists in the mechanical pulp.[11] Consequently, it is possible that the solvents are binded by NBW in micropores within the cell wall, which might result in high solvent retention values and might prevent solvent evaporation.

EXPERIMENTAL

In this study, the solvent retention of gravure printed, cellulose fibre based FBB cartonboard with different moisture contents was analysed. We focused on the critical solvents, such as ethanol and ethyl acetate, and on the role and importance of the substrate's moisture content.[12]

The retained solvent amounts are detected by gas chromatography (GC), which is a chemical analysing process that separates chemicals in a complex sample, whereas the sample is vaporised and inserted onto the head of the chromatographic column for the investigation of volatile compounds. The headspace-gas chromatography (HS-GC) process consists of two steps. First, the sample is placed in a vial having a gas volume above it and the vial that is closed, then thermostated at a constant temperature in HS oven until equilibrium is reached between the two phases. An aliquot of the vial's gas phase (HS) is then introduced into the carrier gas stream, which carries it into the column, where it is analysed. The two steps of HS-GC are illustrated in Figure 5.[13,14]

Printed samples with three different moisture content 6.7% (Board A), 6.9% (Board B) and 8.3% (Board C) have been prepared for solvent retention measurements, done on Agilent 6890N gas chromatography equipment in four time periods: immediately, 1 day, 7 days and 14 days after printing. 50 cm^2 samples are cut from the printed material, rolled with the printed side in and then placed into the HS vial rapidly. 1 ml matrix solution is added into the vial and closed tightly, then heated up to the specified temperature in order to establish phase equilibrium. The vapour phase sample is introduced to the gas chromatograph column via the transfer line; the sample is separated, detected and quantified by FID. GC machine setup parameters: column: 30 m, 0.53 mm i.d., 5.0 mm non polar phase; carrier gas: Helium, pressure optimised for peak resolution; injector: split injection; detector: FID. Injector and detector temperatures were optimized. Method configuration: last vial 40, headspace mode constant; oven, needle and transfer temperatures were optimized ranging from 100 °C to 150 °C; GC cycle, thermostat time, headspace pressure, pressurisation time and injection time were optimized in order to get a sufficient amount of solvent compounds for GC detection. The concentrations of the solvents retained on the printed packaging materials are reported in mg/m^2.

Over the years, major international food manufacturing companies have established limits of acceptable solvent retention levels in their specification sheets, including limits for ethyl acetate, a very important odorous solvent used in the gravure printing technology. Solvent retention results were compared with solvent retention tolerances provided by the food industry, as shown in Table 2.

The FBB type, fiber based, top side coated, 215 g/m^2 cartonboards with CTMP in the middle layer have been test printed by a Bobst Lemanic 650 rotogravure machine for solvent retention analyses. Table 3 shows the press setup and printing parameters. Ink types and supplier, premixed solvent ratio in ink, viscosity, solvent types and amounts are presented in Table 4.

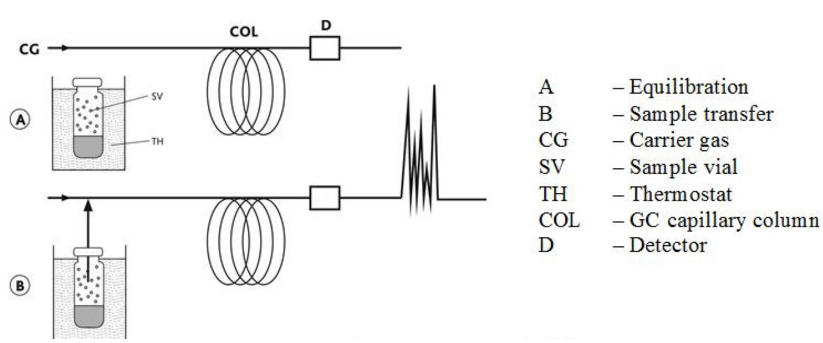

Figure 5: HS-GC principle

Table 2
Solvent retention tolerance

Solvent type	Ethanol	Iso-propanol	Propanol	Ethyl acetate	Isopropyl acetate	N-propyl-acetate	Ethoxy propanol	Total retention
Tolerance, mg/m^2	no limit	max. 5	max. 5	max. 5	max. 10	max. 5	max. 10	max. 30

Table 3
Printing parameters

Printing unit	Cylinder type	Speed, m/min	Drying temperature, °C	Pressure, kN
1	Laser engraved		50	17
2	Mechanically engraved	100	50	16
3	Full tone varnish		125	16

Table 4
Test print parameters of the inks and solvents

Printing unit	Inks		Viscosity, s	Solvents	
	Type	Premixed solvents		Solvent 1	Solvent 2
1	Basic green	Ethanol free, Ethoxy propanol, Ethyl acetate	17.0	Ethanol 25%	Ethyl acetate 75%
2	Basic blue	Ethanol free, Ethoxy propanol, Ethyl acetate	15.3	Ethanol 25%	Ethyl acetate 75%
3	Varnish	-	-	Ethanol 25%	Ethyl acetate 75%

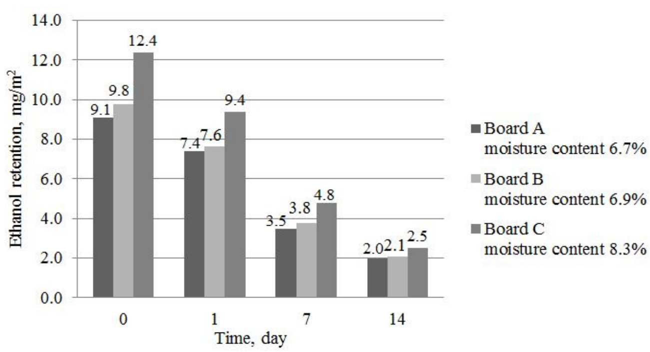

Figure 6: Ethanol retention of cartonboards (A, B and C) with different moisture content, measured at different time intervals after printing

RESULTS AND DISCUSSION

Ethanol retention

The results on ethanol retention of the three cartonboards measured by the GC method are shown in Figure 6. In the solvent retention specification, there is no limit regarding ethanol retention, therefore it should not be problematic. However, ethanol retention represents a significant part of the total solvent retention, consequently, it is recommended to keep it as low as possible in order to comply with the total solvent retention tolerance (maximum 30 mg/m^2), as requested by the food industry standards. Ethanol has a relatively fast evaporation speed and the experience has shown that even a high amount of ethanol retained by the printed blanks is acceptable and within the tolerance level 1-2 days after printing. All the detected individual solvents retained have to within the tolerance level, considering the total retained solvent limitation. For all the three boards tested, the retained ethanol content was relatively low and acceptable. It was found that when the base board moisture content was low, the retained ethanol content of the printed sample was also low.

Ethyl acetate retention

Figure 7 shows that ethyl acetate is a more critical solvent in terms of retention levels, because it has a low evaporation speed, as demonstrated during the test prints: it took even up to two weeks for high amounts of ethyl acetate retained by the printed blanks to decrease to the specified level.

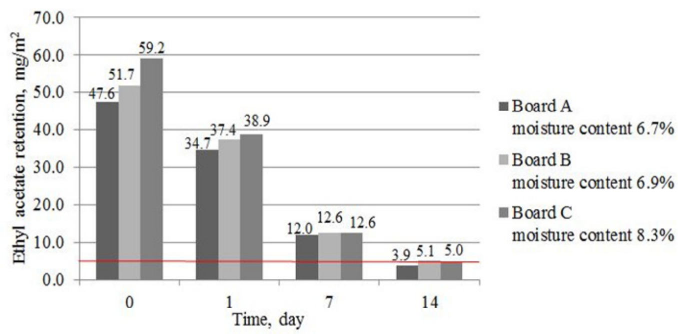

Figure 7: Ethyl acetate of cartonboards (A, B and C) with different moisture content, measured at different time intervals after printing

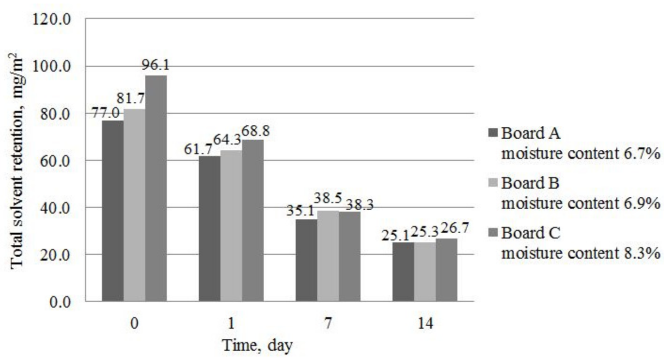

Figure 8: Total solvent retention of cartonboards (A, B and C) with different moisture content, measured at different time intervals after printing

The ethyl acetate retention amount is not allowed to be more than 5 mg/m^2 when the packaging material is delivered to the end-user. In our case, all the results were significantly higher than the tolerance levels right after printing, but board A with 6.7% moisture content achieved the lowest result out of the three boards tested. The absorption of ethyl acetate in the driest sample was by 11.6 mg/m^2 lower than in the wettest sample right after printing. Seven days after printing, the amount of the retained ethyl acetate decreased appreciably for all the test boards. However, an acetate level of 12.0-12.6 mg/m^2 is still beyond the tolerance level, thus the printed material is not ready to be delivered. The retained ethyl acetate reached an acceptable level 14 days after printing. Nevertheless, it was concluded that the lower the board moisture content, the lower the ethyl acetate retention of the printed packaging material is.

Total solvent retention

Ethanol, ethyl acetate, 1-ethoxy-2-propanol and 2-ethyl-1-hexanol were detected by GC, consequently the retained amounts of these solvents were summed up as the total solvent retention of board samples (A, B and C). Multiple measurements of total solvent retention were performed for all test boards right after printing and the results were compared with the allowed maximum amount of 30 mg/m^2. The total solvent retention for board A with the lowest moisture content was by 19.9% lower than for board C with the highest moisture content. In this case, the main solvent with this remarkably high total solvent retention was ethyl acetate. Figure 8 shows a dynamic solvent release rhythm for all the solvents retained, i.e. the retained total solvent amount of all the test boards decreased measurably 7 days after printing. However, the total solvent retention level is still beyond the specified limits for all the boards tested. 14 days after printing, the retained total solvent level became acceptable for all the boards. For the total solvent retention, the conclusion was the same as in the case of the individual solvents analysed, i.e. the lower the board moisture content, the lower the total solvent retention of the printed packaging material is.

CONCLUSION

The aim of this study was to evaluate the importance and the effect of moisture content in fiber based FBB packaging board on the retention and release of solvents used in gravure printing. The residual solvent content of the printed samples with three different moisture contents was measured at four time intervals: immediately, 1 day, 7 days and 14 days after printing. The work had a special focus on the critical solvents (ethanol and ethyl acetate), but total solvent retention was also assessed.

The results have shown that the driest board sample (A – 6.7% moisture content) gives lower solvent retention than the wettest sample (C – 8.3% moisture content): the retention was on average by 23.7% lower for ethanol and respectively, by 14.3% lower in the case of ethyl acetate. Total solvent retention corresponds to the measured individual solvent retention levels.

Both individual and total solvent retention of boards A, B and C reached the acceptable level 14 days after printing, nevertheless solvent retention decreased dynamically. It turned out that the board with lower moisture content had lower ethanol and ethyl acetate retention, as well as a lower amount of total retained solvents. Consequently, it has been concluded that a decrease in board moisture content has a notable effect on solvent retention in 2 ways: the absorbed solvent amount decreases and solvent evaporation dynamics increases.

In this study, all analysed boards had the moisture content lower than 10%, therefore it may be assumed that only non-freezing water existed in the pulp. Thus, it is possible the solvents were bound in the micropores within the cell wall, which might result in high solvent retention values. As a conclusion, board moisture content has to be considered as an important variable in solvent retention analysis.

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