https://doi.org/10.24867/GRID-2022-p9 Professional paper

DEVELOPMENT OF NEW UV LED CURABLE INKJET VARNISHES

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Abstract: *We have prepared three UV curable varnishes for inkjet printing that can be cured by UV LEDs (365–395 nm). The advantages of UV LEDs compared to medium pressure mercury lamps (conventional source of UV radiation) are lower energy consumption, possibility of immediate switching on/off, no IR radiation, no ozone generation and are mercury free. UV LEDs cannot effectively (or at all) cure formulations designed for mercury lamp curing. Developed UV varnishes enable the creation of special varnish effects on printed substrates (including 3D) thanks to partial curing with UV LEDs. Evaluated properties of prepared varnishes were viscosity, surface tension, reactivity, long-term stability and printability. The printing properties of prepared UV curable varnishes were tested on commercially available inkjet printing machine (Spotmatic 36, KOMFI). The cured varnish layers (thickness 20 and 40 μm) were evaluated in terms of mechanical properties (adhesion, elasticity) and optical properties (yellowness). Namely, the study of mechanical properties included the evaluation of adhesion by Tape test, quality of the varnish layer with respect to cutting and grooving, and elasticity/adhesion of grooved varnish layers after folding (180 °). Results showed that prepared UV LED curable varnishes have very good elasticity and adhesion to various printing substrates and enables further trouble-free mechanical processing of varnished products, such as cutting, grooving or bending.*

Key words: inkjet, varnish, UV LED, curing, mechanical properties

1. INTRODUCTION

UV curable inks and varnishes are often used in the printing industry due to the advantages that these inks/varnishes exhibit. The most significant advantage includes very fast curing (for radical polymerization it is a fraction of a second), which allows immediate processing of the printed materials in the finishing. UV curable inks/varnishes have very good chemical and abrasion resistance. From the point of view of mechanical properties, the cured layers can be flexible or, on the other hand, very hard, depending on the choice of binder system (mixture of reactive monomers and oligomers). A significant advantage is also the lower energy consumption needed for curing compared to inks/varnishes drying by solvent evaporation. UV curable inks/varnishes can be used to print a wide range of materials, such as various types of papers, cardboards, plastics, metals, etc. UV-curable inks/varnishes are used in almost all printing techniques, most often in offset printing, flexographic printing, screen printing and inkjet printing.

Inkjet printing has become the major printing technology for sign and display applications, as are posters, billboards, etc. The using of UV curable inkjet systems is the fastest growing technology within this segment (Mondt & Graindourze, 2015). According to Smithers Pira, the UV inkjet printed products market sector was forecasted to reach almost 16 billion USD (in 2008 it was 4 billion USD) (Lee, 2015). The CAGR (Compound Annual Growth Rate) for UV inks sales between 2007 and 2020 was + 4.5 % (Engberg, 2021).

Two curing mechanisms may be used to polymerize UV curable formulations. The more often used is free radical polymerization and the second one is cationic polymerization. Free radical polymerization currently predominates because of its low cost, wide selection of usable components (monomers, oligomers, and photoinitiators) and faster curing (fraction of second). The main disadvantages of free radical polymerization are mainly oxygen inhibition and lower adhesion to common polymeric substrates, as are PE, PP, or PET. Compared to this, cationically polymerizable systems are not inhibited by oxygen and their adhesion to polymeric materials is generally higher. The disadvantages lay in higher cost of ink formulations, slower curing speeds (final properties of the cured film are achieved within 24 hours after UV exposition depending on ink/varnish formulation, UV dose/irradiation and ambient conditions) and inhibition caused by impurities as bases and high humidity (Green, 2010).

Hybrid polymerization is formed by a combination of free radical and cationic polymerization. Both mechanisms can run simultaneously or consequentially. Ink formulation contains typically both types of monomers/oligomers polymerizable by free radical or cationic mechanism and photoinitiators starting both polymerization reactions. Main advantages of hybrid polymer systems consist of combination of the properties of the constituent polymers, increased curing speed, faster development of the final properties of cured films, lower sensitivity to inhibition by air oxygen and improved mechanical properties of the produced films (Jašúrek, 2008; Lin & Stransbury, 2003).

There are a lot of parameters that need to be considered in the UV inkjet ink/varnish formulation. Among the main problems belongs the choice of suitable monomers/oligomers according to the final mechanical film properties, their reactivity, compatibility, toxicity and viscosity. Inkjet inks/varnishes have lower viscosity than conventional flexography, screen or offset printing inks. Typically, the optimal viscosity of UV inkjet inks for industrial printing heads is between 10 and 15 mPas at 40 °C (Mondt & Graindourze, 2015). Due to the low viscosity and small volume of drops ejected from the printheads, the atmospheric oxygen can easily diffuse into inks/varnishes causing serious problems with surface curing. Other parameters that must be considered when formulating inkjet inks are optimization of initiation system, optimization of formulation with additives (in the case of inks also addition of pigments/dyes), curing speed, oxygen/base inhibition, adhesion, long-term stability, printing quality/stability, yellowness (important mainly in UV-LED curing of varnishes), etc.

The most commonly used radiation source for curing of UV curable inks and varnishes are medium-pressure mercury lamps. They are relatively cheap and are produced in various lengths and outputs. Another advantage is emission of UV radiation in the form of emission bands throughout the UV region (UV-A, UV-B and UV-C). Disadvantages include short lifetime (approximately 1500 hours), produce large amounts of infrared radiation, need to be cooled, produce ozone and contain toxic mercury. Relatively new source of UV radiation are UV-LEDs (diodes emitting radiation in UV region). UV-LEDs began to be used in printing industry about 15 years ago. The advantages of UV LEDs compared to medium pressure mercury lamps are lower energy consumption, possibility of immediate switching on/off, no IR radiation, no ozone generation and are mercury free. Disadvantages include higher cost and radiation emission in a narrow region of the spectrum (emission band width around 30 nm). UV LEDs cannot effectively (or at all) cure formulations designed for mercury lamp curing and inks/varnishes have to be reformulated for curing with UV-LEDs.

The aim of this work was to develop hybrid UV LED curable inkjet varnishes with better mechanical properties (higher adhesion and elasticity) than commercially available ones (free radically polymerizable).

2. MATERIALS AND METHODS

Prepared hybrid inkjet varnishes (3 modifications) consists of acrylate, oxetane, and vinylether monomers. The initiation system consists of initiators and sensitizers of free radical and cationic polymerization. Additionally, stabilizers of premature polymerization for each polymerization mechanism and wetting agent were added. First prepared hybrid inkjet varnish (HV1) is partially cured by UV LED (365, 385, or 395 nm) and final curing is ensured by UV exposition with medium pressure mercury lamp. Another two hybrid varnishes (HV2 and HV3) are fully cured with UV LED sources (365, 385, 395 nm).

The hybrid inkjet varnishes were compared with two commercially available ones. The first varnish is K-flex UVV H-cure from the company Kao Chimigraf (cured by medium pressure mercury lamp) and the second one is KomfiFlex LED Alfa N varnish from company Nazdar Ink Technologies (cured by UV LED or medium pressure mercury lamp). A matt laminated cardboard (polypropylene foil) was used as the printing substrate for printing and evaluating of mechanical properties of varnishes. The surface free energy of the printed material was adjusted by corona treatment (38 mN/m).

Surface free energy of varnishes was evaluated by Du Noüy Ring method with tensiometer K6 (Krűss). The measurements were performed at room temperature (22 °C). The measurement accuracy is 0.5 mN/m. The rheological properties of varnishes were measured by rheometer RotoVisco 1 (HAAKE) at 40 °C with measuring system DG43 up to the shear rate 3 000 s^{-1}.

Inkjet varnishing machine Spotmatic 36 (KOMFI) was used for printing of all tested varnishes. As UV sources were used UV-LEDs emitting at 365 nm or 395 nm (Shenzhen Bird UV Technology, irradiance 10 W/cm^2 and 16 W/cm^2 respectively) and medium pressure mercury lamp (120 W/cm). The thickness of the printed layers was 20 and 40 μm.

From the mechanical properties were evaluated the adhesion of printed layers to matt laminated cardboard by Tape test (Tesa tape 4104), the quality of the varnish layer after cutting, and adhesion/elasticity of varnish layer after grooving by machine GPM 450 SA (Cyklos Choltice) and bending varnish substrate at the point of the groove by 180°. The grooving tool had a U profile (depth 0.7 mm, width 1.4 mm).

Optical properties (yellowness) were evaluated by spectrophotometer X-Rite 530. Measured parameters were L^*, a^*, b^* coordinates of CIELAB colour space. From these coordinates was calculated the colour difference ΔE (Equation 1). The reference material for the calculation of ΔE^* was white paper with laminating film made of PP, which was used for printing of varnishes.

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

ΔL^* is the difference of coordinates L^* of the measured sample and the reference
Δa^* is the difference of coordinates a^* of the measured sample and the reference
Δb^* is the difference of coordinates b^* of the measured sample and the reference

3. RESULTS AND DISCUSSION

Three inkjet varnishes polymerizing by hybrid mechanism (combination of free radical and cationic polymerization) were prepared. The first one (HV1) is partially cured by UV LEDs (365, 385, or 395 nm) and the final curing is ensured by exposition with medium pressure mercury lamps. The second one (HV2) and the third one (HV3) are fully cured by UV LEDs.

The surface free energy of the prepared hybrid varnishes was 24.0 mJ/m^2 (HV1), 25.0 mJ/m^2 (HV2), and 24.5 mJ/m^2 (HV3). Both commercially available varnishes have surface free energy 23.5 mJ/m^2.

The dynamic viscosity of all tested varnishes was evaluated in the range of shear rates 100–3000 s^{-1} at 40°C. The dynamic viscosity in all cases slightly increases with increasing shear rate (HV1 10.2–12.1 mPas, HV2 9.1–10.8 mPas, HV3 9.5-11.1 mPas, KomfiFlex LED Alfa N 11.4–12.6 mPas, K-flex UVV H-cure 9.7–11.8 mPas).

The stability of the prepared hybrid varnishes was tested at room temperature for 3 months and at elevated temperature (60°C) for 10 days. The stability of the hybrid varnishes was very good for all samples and only a slight increase in viscosity (1–4 mPas) occurred during testing.

The printing speed differs due to the different need for irradiation to ensure a dry and nonsticky film. HV1 can be printed with printing speed 12 m/min (medium pressure mercury lamp), HV2 with 6 m/min (UV LED 395 nm), and HV3 with 20 m/min (UV LED 395 nm).

The adhesion and elasticity of the prepared hybrid varnishes and two commercially available ones was evaluated by three methods. The first one was Tape test (Tesa tape 4104). Adhesion of varnishes to matt laminated cardboard was tested for layers with thickness 20 and 40 μm.

All hybrid varnishes have very good adhesion to matt laminated cardboard. During the tests, no damage of hybrid varnish layers by Tesa tape 4104 was observed for both varnish thicknesses. In the case of commercially available varnishes, approximately 30 % of the tested samples were damaged (varnish layer 20 μm) regardless of varnish type. When testing thicker layers (40 μm), only a few samples (less than 10 %) were damaged by Tesa tape and the adhesion of commercially available varnishes with this thicker layer was only slightly worse than the hybrid ones.

Second method was evaluation of the quality and adhesion of the varnish layer after cutting. All tested varnishes (HV1–HV3 and both commercially available ones) were undamaged after cutting, but there was a significant difference in adhesion at the edge of cut. The hybrid varnishes (HV1–HV3) exhibited very good adhesion at the edge of the cut (no peel off), while both commercially available varnishes were easily peeled off.

The third method was focused on the evaluation of the adhesion/elasticity of varnished layer on matt laminated cardboard after grooving and bending the substrate at the point of the groove by 180°. After grooving, no peeling off was observed for all tested varnishes. Difference between varnishes was observed after substrate bending. Hybrid varnishes (thickness 20 μm) showed no defect at the groove and bending (Figure 1a). With a thicker layer (40 μm), approximately 25 % of the samples with hybrid varnishes HV1 and HV2 were damaged (slight cracking of the varnish layer or partial peeling off) and approximately 75 % for HV3. The commercially available varnishes (thickness 20 μm) exhibit peeling off after bending (approximately 30 % of samples) and in case of thicker layer (40 μm), peeling off and also cracking of the varnished layer (more than 75 % of samples, Figure 1b, c). The poorest results of adhesion in bending tests exhibits varnish K-flex UVV H-cure from Kao-Chimigraf.

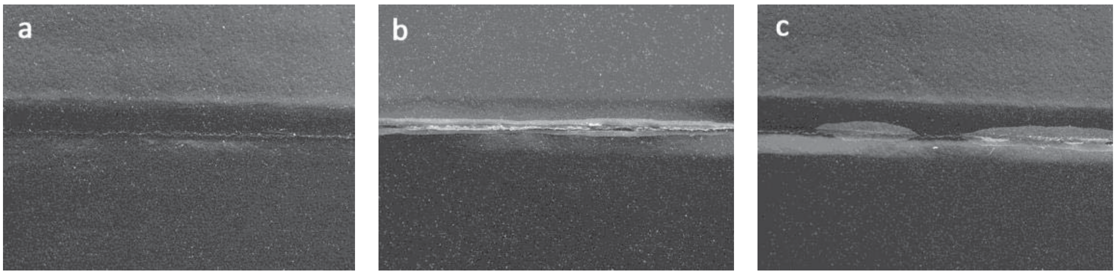

Figure 1: Defects of varnish layer (40 μm) after grooving and bending, a – Hybrid varnish HV1, b – K-flex UVV H-cure from Kao Chimigraf, c – KomfiFlex LED Alfa N from Nazdar Ink Technologies

Yellowness of the prepared hybrid varnishes (HV1 and HV2) was better than the commercial ones. Yellowness of HV1 and HV2 was mostly in range of ΔE^* 2.5–4 (thickness 20 μm) and 4–6 (thickness 40 μm). Commercially available varnishes have ΔE^* around 4–7 (20 μm), respectively 8–11 (40 μm). Hybrid varnish HV3 has ΔE^* 7–8, respectively 14–15. Yellowness of hybrid varnish HV3 is higher and is suitable to use it for printing of thinner layers, approximately till 15 μm. Compared to this, with HV1 and HV2 is possible to create special varnish effects with a thickness of tens (hundreds) of micrometers with low yellow tint (Figure 2).

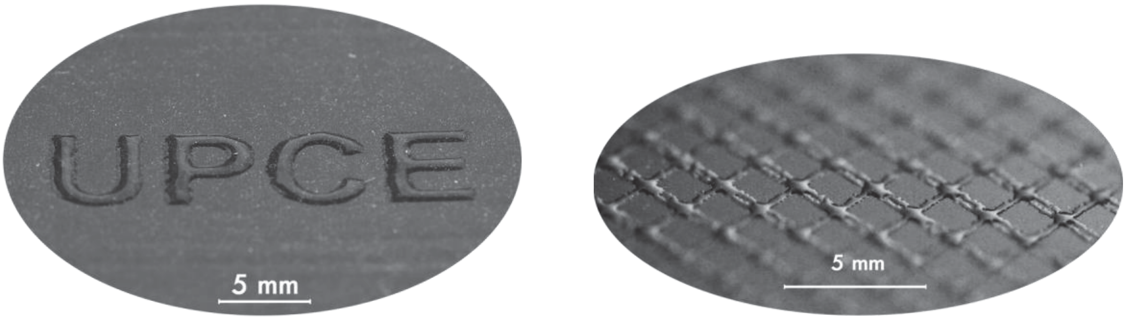

Figure 2: Examples of varnish effects with Hybrid varnish HV1

5. CONCLUSIONS

Three inkjet varnishes polymerizing by hybrid mechanism (combination of free radical and cationic polymerization) were developed. The first one (HV1) is partially cured by UV LED (useful for spot varnishing and creation of special varnish effects and 3D structures) in the range of tens or hundreds of micrometers. Final curing is ensured by exposition with medium pressure mercury lamps. The second one (HV2) is hybrid varnish that can be cured fully with UV LED. The main advantage of HV1 and HV2 is their high elasticity, very good adhesion, and low yellowness. The third one (HV3) is also fully cured by UV LED and its advantage is the possibility to print with high printing speed (20 m/min). This varnish has also very good adhesion. Due to lower elasticity and higher yellowness, it is not suitable for printing thicker layers (> 15 μm). All developed hybrid varnishes have good long-term stability at room and elevated temperature (60 °C) and show stable behavior during printing.

6. ACKNOWLEDGMENTS

This work was supported by the Technology Agency of the Czech Republic, project No. TP01010012.

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