Digital printing

Advances in the digital application of polyurethane based coatings and adhesives

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Abstract

Digital printing is visibly gaining importance as a more sustainable application technology for coatings and adhesives. Benefits are obvious: no overspray, less waste, enabling automation and the possibility to efficiently customize properties on a dot-per-dot scale even for small production batches, only to name a few.

Digital application technologies typically require advanced formulations and force a re-evaluation of the suitability of standard raw materials employed. This can be achieved either by adaption, substitution or new developments.

In this contribution, we give an overview on how the versatility of polyurethane based raw materials and formulations makes them the material class of choice to meet the novel requirements of modern digital coatings and adhesives application technologies. Practical examples, challenges and opportunities in the case of automotive, textile and sports & leisure applications will be shown and discussed.

Introduction

The coatings and adhesives world is changing. Higher demands towards increased sustainability, improved industrial hygiene, less production waste and a fully digital manufacturing process are clearly recognizable. For innovative businesses along the value chain - including OEMs, coating and adhesive manufacturers as well as raw material suppliers - the digital application of coatings and adhesives is a logical next step while further offering a more granular control of production processes and a greater flexibility to react to changing demands.

Looking at the state of the art of application technologies for coatings and adhesives, spraying, brushing or screen printing are still predominant in the industry and have largely pinnacled to their full potential. Along with proven and established processes come mature material solutions. Opposing to that, new and unproven disruptive digital application technologies require advanced formulations and more often than not force a reevaluation of the suitability of standard raw materials employed: No easy challenge!

A material of choice for multiple coating and adhesive applications are polyurethane (PU) raw materials. Whereas PUs offer high optical quality, excellent durability and enhanced processability for automotive exterior parts, they are favored in the textile industry due to their high flexibility, soft handfeel and excellent light fastness. In adhesive applications their versatility to adopt to many different substrates and property profiles is highly valued.

Can this proven and highly versatile material class be successfully employed to solve the challenges of digital application technologies? This question will be answered considering three application examples in the area of automotive and textile coatings as well as adhesives for sports & leisure applications.

Overspray-free application of automotive paints

In the automotive industry, spraying is nowadays an enhanced technology and overspray and waste are reduced to a minimum.

Yet, overspray is not eliminated completely and as it is present, masking steps are mandatory to protect adjacent surfaces from paint e.g. in two tone finishes. Overspray-free application methods such as inkjet, valvejet or Dürr's EcoPaintJet[1] will ultimately help to safe energy and reduce waste[2, 3], throughout the production of modern coated car surfaces. As per BMW, if no coating material has to be disposed in a typical automotive coating line due to no overspray, assuming 7000 operating hours, savings in the range of 6000 MWh are possible. Dürr expects up to 25 % less energy per car body while using their overspray-free painting technology. Further, time and therefore costs, can be saved as the masking and demasking becomes unnecessary.

To successfully move towards a truly digital coating application of car bodies, a combination of different digital application technologies can pave the way. Therefore, an example how commercially available valvejet and inkjet technologies can be utilized to produce "digital coating surfaces" together with high-performance PU based formulations, is shown in the following.

The valvejet technology allows to apply materials with dry film thicknesses of 10 µm up to 50 µm. Typically, these thicknesses can only be reached with multiple printing passes when using inkjet technologies. Inkjet, however, is a perfect fit for achieving high resolution images and can play a significant role in adding individual design steps. Hence, a demonstration example was created using a valvejet for the base- and clearcoat application and inkjet for a high-resolution design element, in this case a Covestro logo. In specific, the clear coat is commonly based on PU technology due to its exceptional scratch and weather resistance[4]. Table 1 shows the digitally printed coating formulations.

	Basecoat ink	**Decoration ink**	**Clearcoat ink**
Pos. 1	1K sb state-of-the-art automotive basecoat	OH-functional acrylic resin	OH-functional acrylic resin
Pos. 2	Butyl acetate	Inkjet silver metallic pigment preparation	Polyisocyanate (HDI-Trimer)
Pos. 3		Wetting additives, Butyl acetate	Wetting additives, Butyl acetate
ISO cup 4 mm	28 s	n/a	30 s
Solid content	15 %	6 %	43 %
Targeted Dry Film Thickness (DFT)	10 - 15 µm	ca. 1 µm	35 - 45 µm
Application via	valvejet	inkjet	valvejet

Table 1 Overview of the digitally applied formulations

[1] www.durr-group.com/en/duerrmore/2019/overspray-free-painting-at-audi (accessed 22.10.2021)

[2] www.durr-group.com/en/duerrmore/2019/smart-up-your-plant/no-more-masking-ecopaintjet (accessed 22.10.2021)

[3] www.press.bmwgroup.com/deutschland/article/detail/T0346092DE/nachhaltig-produziert-und-hoechst-individuell:-bmw-m4-kleinserie-entsteht-mit-neuem-lackverfahren?language=de#:~:text=Mit%20der%20Lackierung%20der%20Kleinserie,Produktionsnetzwerk%20der%20BMW%20Group%20erfolgen. (accessed 22.10.2021)

[4] M. Mechtel, T. Hebestreit, European Coatings Journal 05/2021 „Who shines the longest?"

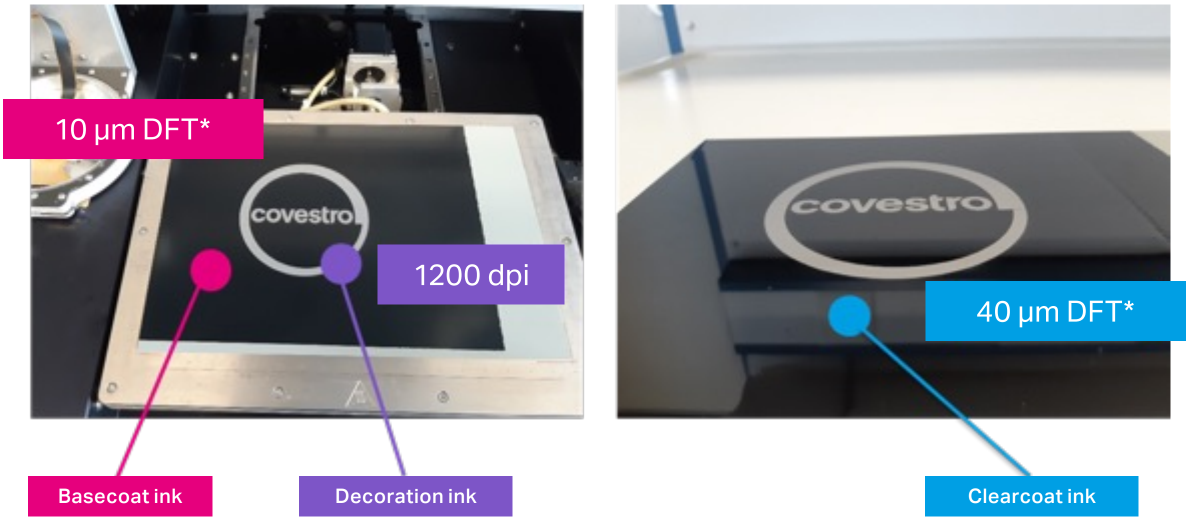


Fig. 1 – Demonstration example of digitally applied automotive coatings. * DFT = Dry Film Thickness © 2021 Covestro Deutschland AG

In Fig. 1 on the left the applied black basecoat (valvejet) with the high resolution Covestro logo printed on top (inkjet) is shown. Subsequently, as seen on the right picture, the clearcoat was applied (valvejet). The obtained printed layers were then benchmarked using wavescan against a surface finish from a trained applicator using HVLP spray (see Fig. 2)

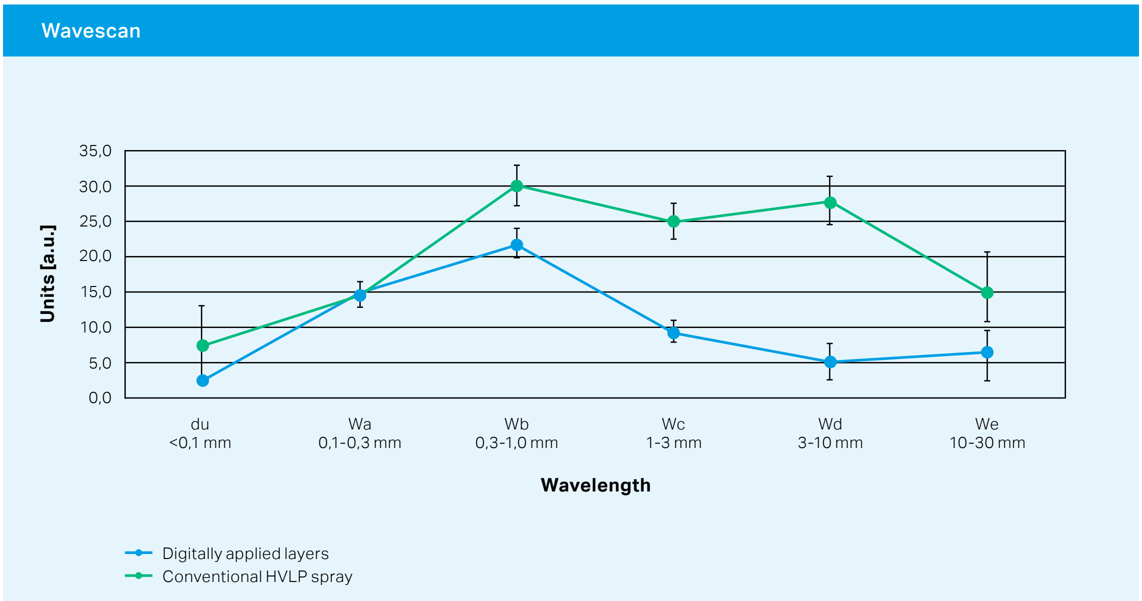
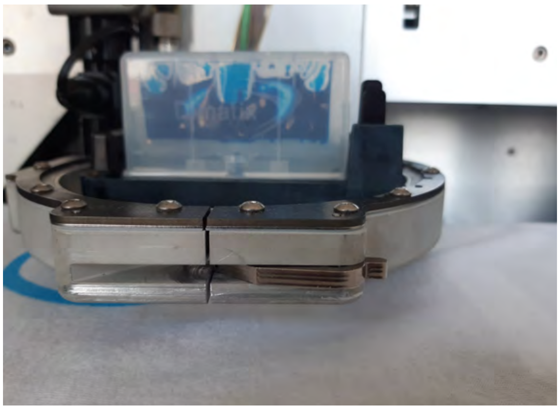


Fig. 2 Wavescan of digitally applied layers in comparison to HVLP manual spray by a skilled applicator. In general, lower values are better

From Fig. 2 it can be concluded that the digital application of the base- and clear coat provides excellent surface finishes. In this particular case the “digital” surface finish shows a better appearance as it has lower dullness and less distortion by longer wavelengths Wc, Wd and We. In addition, the digital application comes with higher design freedom and obviously without the need of masking.

Yet, this is only the start of the race towards a new, more sustainable and more efficient way to apply future automotive coatings. There are still remaining challenges, such as application on complex and vertical surfaces and how to obtain formulations that combine applicability, surface finish and sufficient sagging control in a single pass application.



Combined efforts from raw material suppliers, coating formulators, integrators and OEMs will be necessary to overcome the challenges ahead for truly digital automotive coating applications. Noteworthy, the inkjet world starts to show signs of adaption into the jetting of more complex and higher viscous fluids such as paints. They are currently introducing new printheads that may be very well of interest.[5,6]

[5] www.xaar.com/de/campaigns/high-laydown-eu/ (accessed 26.10.2021)

[6] www.quantica3d.com/ (accessed 26.10.2021)

Waterborne polyurethanes enabling mass-customization in digital textile printing

As of today, more than 85 % of printed textiles are manufactured by using an analogue screen printing technology. However, an increasing trend towards extraordinary short times-to-market, individualization and sustainability drives the revolution of the textile industry[7,8]. A shift towards digital application technologies is observed in the global market considering the intensified use of dye sublimation technologies. The potential for an increase of process efficiency and a more sustainable material usage, taking out an extra step and the cost and waste produced by transfer papers, by employing digital direct-to-garment/--fabric processes is obvious.

A digital application of inks on textile substrates enables a shift of textile finishing steps closer to the customer allowing for shorter times to market, a cost-efficient production of single digit lot sizes and a reduction of waste material up to 85 % in comparison to screen printing[9,10]. According to current forecasts for the digital textile printing market, a CAGR of 19.1 % is expected until 2027 including an increasing demand for novel ink systems[10].

The performance of an ink in both, the digital printing process and the targeted application, is strongly affected by the choice of the binder system. From an application perspective, printed textiles have to be durable under exposure to external factors such as washing, abrasion or scratching while maintaining pleasant haptics (soft handle). However, the trade-off between fastness and handle properties cannot be solved with existing material solutions.

Due to the high film-building ability, excellent mechanical performance, elevated brilliance and soft handfeel, PU raw materials are established as material of choice for screen printing[11]. In order to take advantage of these intrinsic material properties for digital textile printing an adaption of existing and a development of novel PU based material solutions is needed to not only meet application-, but also process-related requirements.

[7] https://de.scribd.com/document/445499441/Gherzi-Digital-Textile-Printing (accessed 28.10.2021)

[8] World Textile Information Network: Market review – digital textile printing, Webinar, October 26th 2021

[9] World Textile Information Network: Digital textile, Issue 01/2021

[10] www.texintel.com/press-room/allied-market-research-report-predicts-that-the-global-digital-textile-printing-market-will-reach-88-billion-by-2027-at-191-cagr (accessed 28.10.2021)

[11] Waterborne Polyurethane Technology for Textile Printing and Coating – Experience sharing from Covestro INSQIN®, Webinar, www.youtube.com/watch?v=qlU9Y52s47c (accessed 5.11.2021)

In order to digitally print using an inkjet with a piezoelectric drop-on-demand printhead onto a textile substrate, both, the jetting of the ink as well as the drop spread on the substrate need to be monitored. Amongst others, a stable jetting of an ink throughout the entire time of processing requires printhead dependent viscosities ranging from 3 - 14 mPas. This results in a limited use of PU binder systems suitable for textile applications, which typically exhibit viscosities between 50 - 500 mPas. However, an elevated usage of binder systems leads to increased fastness properties. Thus, identifying the theoretical maximum amount of a binder system in the formulation is of high relevance to create durable printed textiles. To avoid clogging of nozzles in the printhead, the mean particle size of the binder should not exceed 250 nm, whereby a lower particle size leads to better jettability. In addition to the binder system, the ink formulation contains a humectant to reduce evaporative losses at the printhead. Since higher amounts of humectants such as propylene glycol result in increased curing times, a theoretical minimum should be targeted in the formulation without reducing the process stability. Wetting agents are added to the formulation to reduce the dynamic surface tension allowing for a stable drop formation at the nozzles.

Assuring the desired drop spread of an ink on the textile substrate is impacted by the viscosity of the ink after the rapid reduction of the shear rate as well as surface modifying additives. Once a drop has spread on the substrate, the durability has to be ensured. Using a hardener such as a blocked polyisocyanate which can be activated at elevated temperatures subsequent to the printing process leads to elevated fastness properties. The effect of the hardener is supported by a wax emulsion which protects the surface of the remaining pigments. Pigment pastes or particles are added to the formulation to create the desired design or functional effects.

PU binder systems in combination with blocked polyisocyanates (ink formulation example indicated in Table 2), have proven to enable both, good jettability combined with a high wash and crock fastness as well as abrasion resistance.

Component		**Amount [wt%]**
Pigment	Waterbased pigment paste	20
Binder	Waterborne polyurethane dispersion	17.4
Humectant	Propylene glycole	19.6
Humectant	Preparation of a modified urea	5
Wetting agent	Alcohol alkoxylates	1
Hardener	Blocked polyisocyanate	3.5
Surface protection	Non-ionic emulsion of an oxidized HD polyethylene wax	4
Solvent	Water	29.5

Table 2 Formulation guideline of a pigment ink formulation for digital textile printing based on polyurethane and isocyanate material solutions

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11 Waterborne Polyurethane Technology for Textile Printing and Coating – Experience sharing from Covestro INSQIN®, Webinar, www.youtube.com/watch?v=qlU9Y52s47c (accessed 5.11.2021)

Due to the high flexibility of the PU binder system, a soft handle is achieved. A controlled drop spread of a pigment ink formulation based on a waterborne polyurethane dispersion (PUD) resulting in high edge sharpness and color intensity is shown in Fig. 3 A).

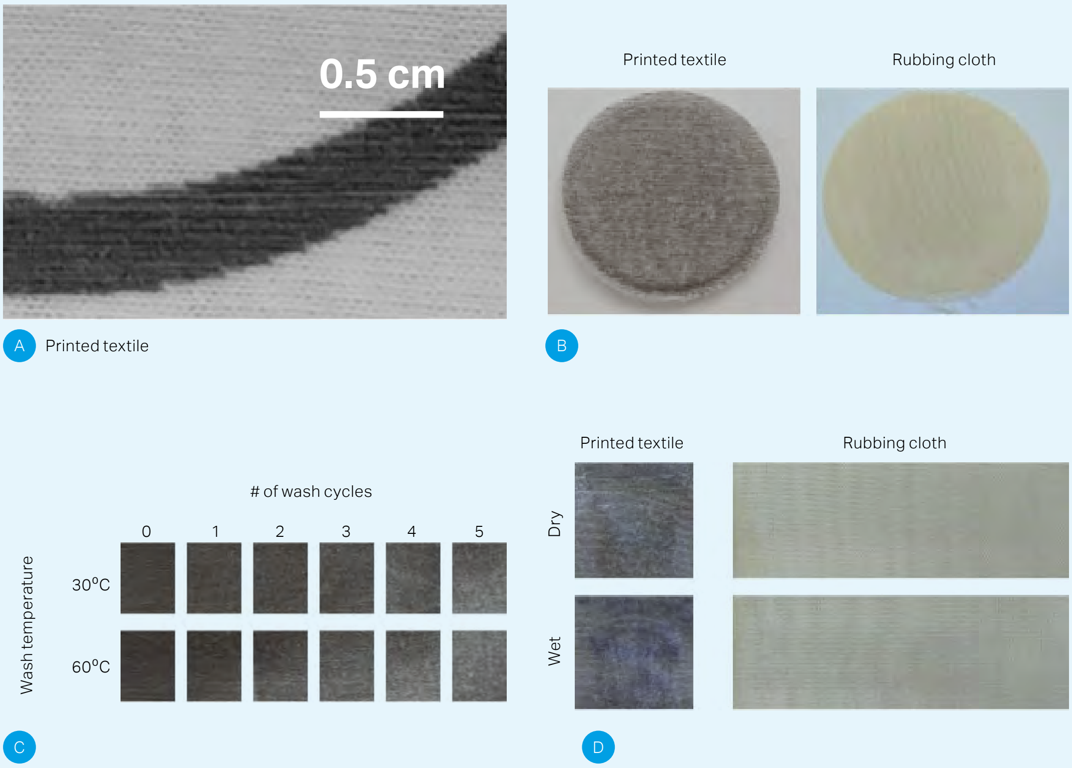


Fig. 3 A, B, C and D

Fig. 3 Digitally printed cotton knitted textile using an ink formulation based on INSQIN® waterborne polyurethane dispersion with a) precise drop spread, b) elevated wash fastness even at 60 °C after five wash cycles in accordance with DIN EN ISO 6330, c) stable dry and wet crock fastness after 50 turns following DIN 55654, d) high abrasion resistance after 10 k turns following DIN EN ISO 12947 © 2021 Covestro Deutschland AG.

Fastness properties of the digitally printed textiles are displayed in Fig. 3 B) – D). Even after five wash cycles at 60 °C only minor changes in the color intensity are observed. The crock fastness under dry conditions is excellent after 50 turns, a slight decrease in the fastness is monitored under wet conditions. Given the excellent abrasion resistance after 10.000 turns, the printed textiles prove to be applicable to a variety of different areas.

Hence, PU based raw materials have proven to be jettable via inkjet resulting in printed textiles for which the trade-off between fastness and handle properties is resolved.

Digital and automated application of novel polyurethane based adhesives

The use of PU based solvent and waterborne adhesives in the production of sports- and leisure goods has played a major role since decades due to their excellent adhesion on various substrates, high initial bond strength, excellent wetting, adjustable tack-life and the possibility to be applied via contact and/or heat activation bonding. A typical production process foresees four major steps: Firstly, the liquid adhesive is applied onto the (primed) surfaces, followed by a drying step with subsequent heat activation and lastly contacting of the materials by pressing.

With the industry sector being subject to increasing consumer demands for sustainable solutions, especially waterborne PUDs are the material of choice. Yet, their application is still in most cases a manual brushing process.

Printable adhesives have therefore been the target of considerable R&D efforts since these allow for highly precise application of glue and enable customization of bond lines paired with the possibility to design a fully automated production process. Especially the printing of PU based adhesives with valvejet technology is favorable as solid layer thicknesses of 30 µm to 100 µm are achievable, fitting well to the requirements of the industry.

So far, the use of state-of-the-art solvent or waterborne PU adhesives in inkjet or valvejet applications has suffered from limited process stability due to evaporation and film formation inside and outside of the printer nozzles.

Hence, novel high solid hybrid water-/solventborne formulations with good shear stability and good resolubility reduce nozzle clogging while providing surprisingly low viscosities at a comparably high solid content thusallow for low head maintenance and good printability when used with valvejet printing.

The polymers depicted in this study are thermoplastic, aliphatic and high molecular weight polyester PUs. Their high molecular weight is responsible for a good initial peel strengths, whereas their open time can be adjusted by the crystallization speed of the polyester employed. For the formulation of the adhesive, the solid polymers were dissolved in a solvent/water mixture, hence combining the good wetting and fast drying properties known from solventborne adhesives. At the same time the solvent content was reduced to more than halve compared to typical solventborne formulations. If the application demands increased heat and chemical resistances of the final bond, commercially available polyisocyanates are well compatible with the novel hybrid formulations.

Maintaining a high solid content for the printable adhesive is a challenge due to their high molecular weight and therefore high solution viscosity. It was solved by a careful choice of a good solvent like MEK, acetone or ethyl acetate in combination with a protic co-solvent like water or ethanol being non-solvents for the polymer chains. In suitable combination solid contents of up to 30 wt% were possible with viscosities in the range of 20 mPas to 70 mPas being readily printable (see Fig. 4). These hybrid formulations exhibit one clear benefit over existing waterborne technology, which is their ability to resolubilize formed films avoiding nozzle clogging of the printer. The otherwise highly appreciated film forming properties of commercially successful PUD adhesive formulations made them unsuitable for the high shear experienced in drop on demand printing technologies. Once a film was formed it could not be resolved by any means, thus being incompatible with most jetting and even high precision spraying technologies.

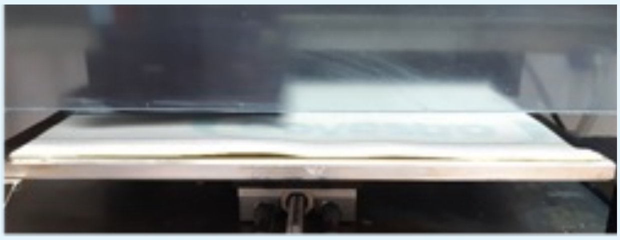
Table 3 compares the hybrid adhesive formulation to a state-of-the-art PU dispersion of comparable molecular weight and composition. The PUD was diluted to a comparable solid content. A microfiber fleece was chosen as substrate and several structures were firstly designed using CAD data and transferred to the printer. Being able to do this means great efficiency gains as processing steps like area marking become redundant. It was not possible to have the PUD printed continuously as the nozzle quickly started to clog which made additional rinsing/ cleaning steps necessary. On the contrary, the hybrid formulation was able to resolubilize itself and thus allowed a stable and continuous printing process for several hours.

	PUD	**Hybrid formulation**
Viscosity [mPas]	10	25
Solid content [%]	20	20
Printing technique	valvejet	valvejet
Resolubility	poor	good
Printing stability	poor	good

Table 3 Comparison of the new hybrid adhesive formulation to a classical PUD

As shown in Fig. 4 the adhesive can be applied on the microfiber surface precisely as seen on the sharp edges, preventing overspray, meaning too much adhesive has been applied and thus becomes visible.

Further material saving can be made as the adhesive is only applied where it is really needed as is exemplary shown in the middle. The example on the right shows the full potential with respect to design freedom without having to worry about overspray or masking. This can be of special interest if sensitive substrates need to be glued like e.g. wearables / electronics onto fabrics.



Ingredient	Amount [wt%]
New polyester polyurethane	20
MEK	20
Acetone	30
Water	30

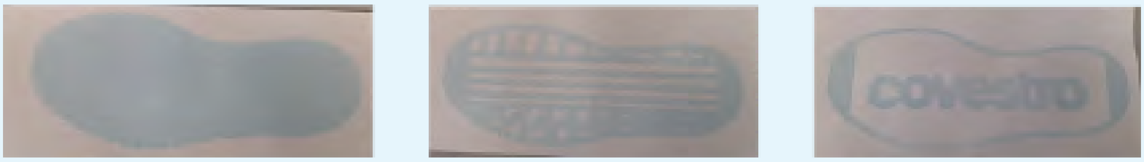
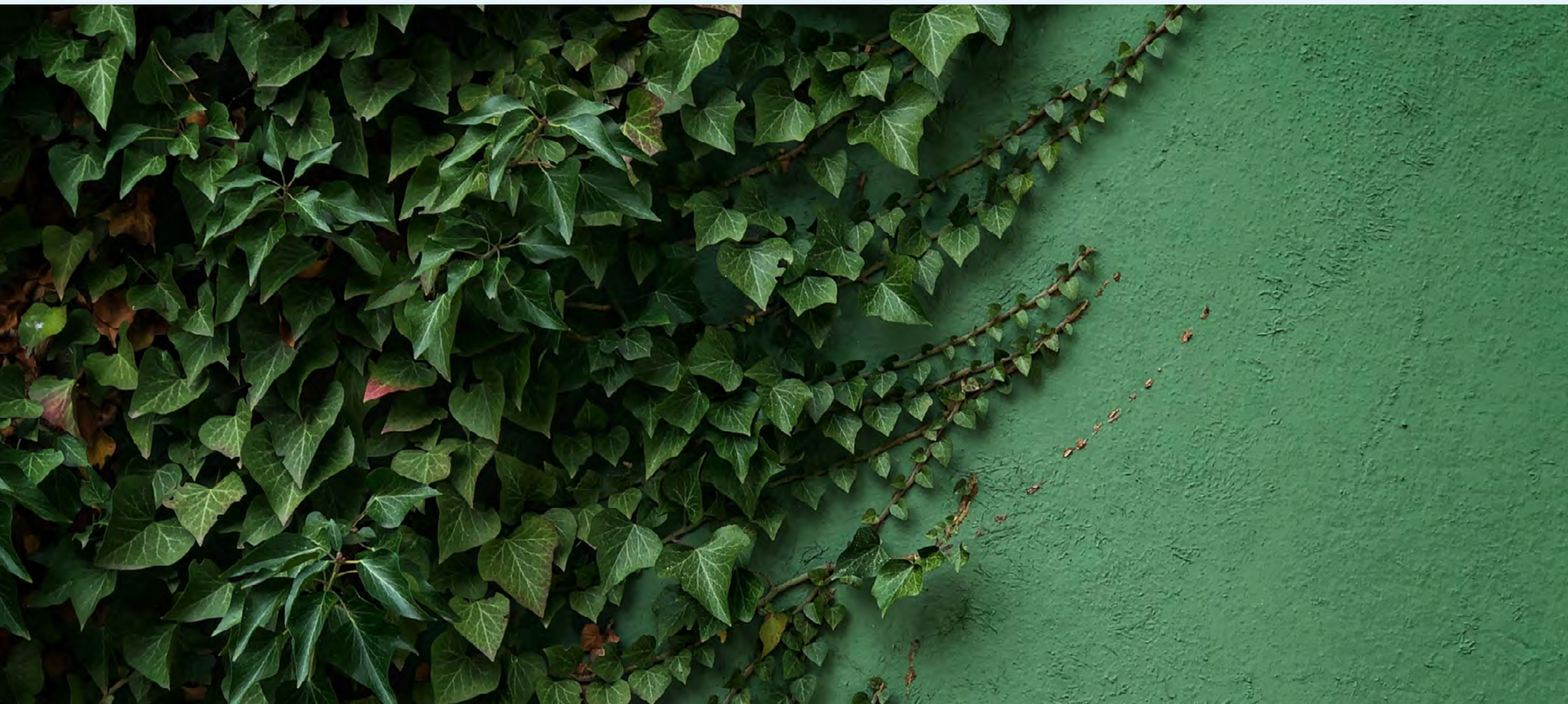


Fig. 4 Printing process of the hybrid adhesive formulation (top) Printing results on a microfibre fleece showing exemplary a common glue application on a shoe sole (left) followed a glue application with individual bondlines (middle) and an example exhibiting a high degree of design freedom (right) (adhesive is coloured for better visibility) © 2021 Covestro Deutschland AG



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Summarizing the above mentioned examples, it becomes clear that a high value lies in the combination of a digital application with the versatility of polyurethane chemistry. Polyurethane based coatings and adhesives elevate the development of digital application technologies by leveraging the potential to reduce costs via automation, less (no) overspray and a more sustainable material use.

Future challenges are in the two major areas of process stability and quality of the applied surface finishes all being inseparably tied to the materials applied. The former include reliability of the applicator, ability to be largely industrialized and ease of maintenance. The latter has to solve the area of conflict between applicable paint/adhesive formulations and the resulting surface qualities. Sagging control on 3D surfaces, edge sharpness and overall appearance will strongly factor into the development of future raw materials and formulations. We believe specifically the polyurethane toolbox offers a great advantage in being able to adopt to and meet the new requirements arising from digital application processes.

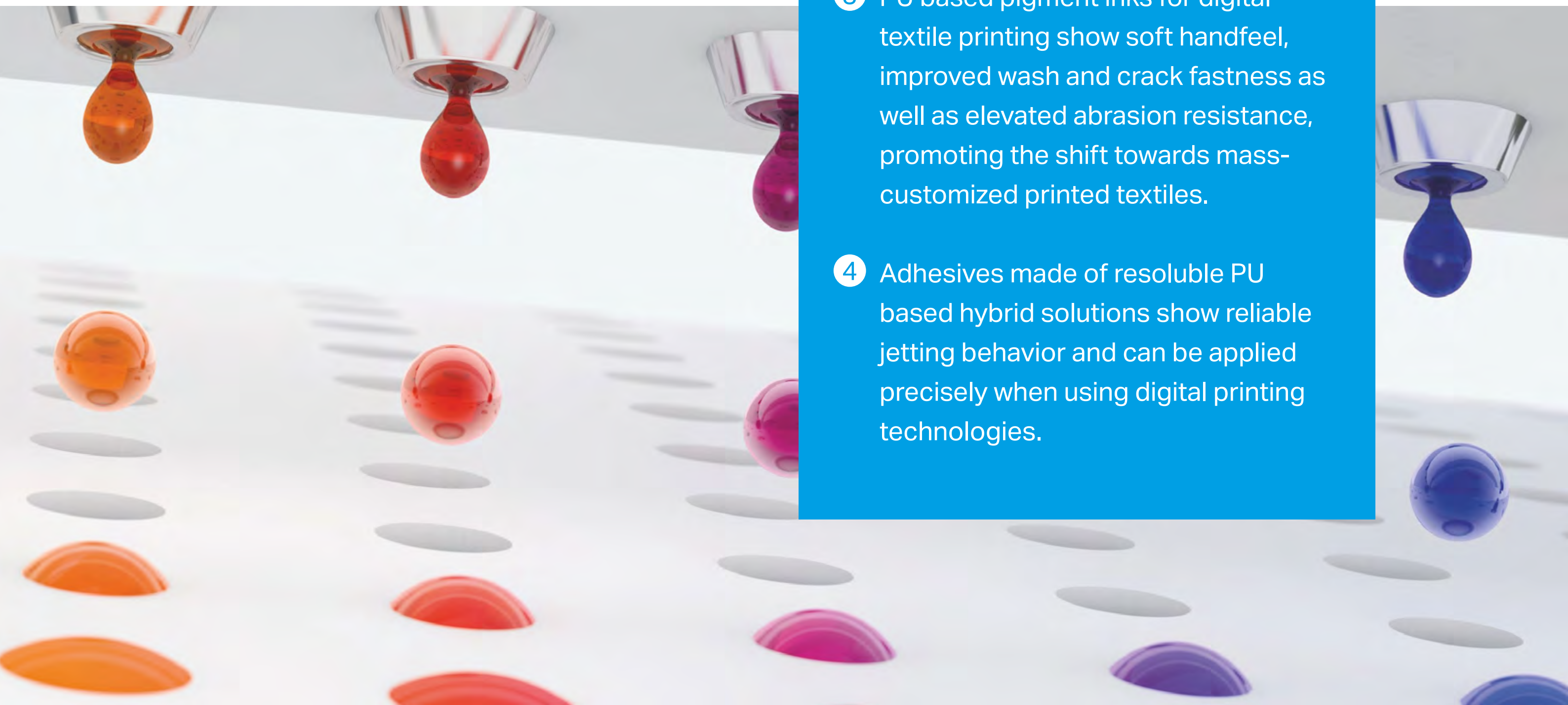
Key results:

① Higher demands in the coatings and adhesives industries towards increased sustainability, improved industrial hygiene, less production waste and greater flexibility in production can be met with digital application technologies.

② Digitally applied base- and clear coats based on PU raw materials have proven to provide excellent surface finishes of automotive exterior components while avoiding the need of masking.

③ PU based pigment inks for digital textile printing show soft handfeel, improved wash and crack fastness as well as elevated abrasion resistance, promoting the shift towards mass-customized printed textiles.

④ Adhesives made of resoluble PU based hybrid solutions show reliable jetting behavior and can be applied precisely when using digital printing technologies.



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[1] Please see the "Guidance on Use of Covestro Products in a Medical Application" document.

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