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VINCENTZ

Synthetic leather without solvents

Polyurethane synthetic leathers are normally produced in a multi-stage process which involves removing toxic dimethyl formamide (DMF) from a solventborne layer, then applying a solventborne wear layer. Solvent-free waterborne PU dispersions with a very high solids content of 60 % and excellent performance have now been produced for this application.

Very high solids dispersions developed for textile coatings

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Every year, more than 500 million square metres of textile materials are coated with polyurethane (PU) to impart a leather-like character. The PU synthetic leather produced in this manner is used, for example, in upholstered furniture and shoes.

The coating process typically used to date has a number of disadvantages: it requires several steps, and most of the raw materials for the production of the material are based on solventborne resins formulated with toxic dimethyl formamide (DMF). New high-solids PU dispersions now make the production of synthetic leather more efficient and more environmentally friendly.

Different processes create'feel' and wear resistance

Synthetic materials have been competing with natural leather for more than 30 years. The typical first step towards forming a PU synthetic leather is a coagulation process: a woven or non-woven fabric is coated with a paste preparation of polyurethane polymerised or dissolved in DMF. It is then passed through water baths with decreasing DMF concentrations and finally through pure water.

A phase transfer process with water converts the PU-based paste preparation into a microporous, sponge-like layer. The precipitation runs slowly from the outside in; water penetrates into the layer and displaces the DMF solvent. Distillation is used to recover the toxic DMF from the process water.The coagulation process results in products with volume and a pleasant handle, but not a leather-like appearance. To obtain a suitable high-quality surface, the coagulated layer is coated with two or more additional layers of solventborne PU raw materials.

Waterborne formulations have had major limitations

This conventional process cannot be sufficiently reconciled with the desire for the lowest possible VOC emissions, since its polar character implies that residual amounts of DMF will usually remain in the material. Legislative VOC directives and the specifications of leading brand-name manufacturers in a variety of industries are expected to become increasingly stringent. Attempts have therefore been continuing for some time to produce porous, thick-layered flat fabrics as synthetic leathers without using solvents.Though waterborne coating systems are, for example, expanding their presence in the wood and furniture industry and are becoming increasingly established for the coating of metal industrial goods, corresponding efforts to achieve coating of textiles have at best met with partial success. The attempts failed mainly due to the inadequate thickness of the layers produced and the unsatisfactory mechanical and chemical resistance properties of the resulting synthetic leather.

Bayer MaterialScience has now succeeded in developing high-solids, fine-particle polyurethane dispersions for the formulation of synthetic leather with high resistance properties. These new aqueous dispersions with solids contents of up to 60 % allow an economic and efficient coating process to be performed on existing equipment.

In contrast to DMF coagulation, this process is entirely free of solvents and toxic substances. The process thus meets the requirements imposed on new materials by leading manufacturers of upholstered furniture, sports goods, textile and automobiles.

Frothed foam replaces solvent displacement process

A fundamental characteristic of natural leather is its microporosity. It has the ability to adsorb and later release water vapour. With the conventional process for the production of synthetic leather, the mixing of DMF and water produces a voluminous, porous product as a result of the coagulation process and the heat generated.A similarly porous layer can also be produced using the frothed foam process (see Figure 1). During this process, air is intensively incorporated into a waterborne PU dispersion to produce foam, in a way very similar to that in which whipped cream is made. Foams are produced at various densities (200800 g/l) dependent on the amount of air entrapped. After drying, these satisfy the demands for softness and resistance in the final material.

Stabilisers, thickeners, crosslinking agents and pigments are added to the foam as needed. Until the development of the new PU dispersions with their increased solids content, however, it was not possible to apply sufficiently thick layers with a relatively high density in a single step.

The advantages of this new technology are primarily economic: energy costs are reduced because smaller amounts of water have to be evaporated. At the same time, machine capacity can be better utilised. Finally, the costs for the storage and logistics of the raw materials are reduced.

Bimodal size distribution is the key to high solids

The challenge of producing a fine-particle PU dispersion with a 60 % solids content quickly becomes apparent when considering the following: even the closest theoretical packing of spheres, for example in a crystal, only fills 74 % of the available space. Pouring spheres of equal size into a loose pile will result in a density of only around 64 %, the experimental maximum for flowable materials.

The new generation of polyurethane dispersions is therefore very close to this physical limit. This minor masterpiece of research was achieved thanks to a clever bimodal distribution of the particles in the dispersion. Simply put: The dispersion contains small spheres that fit into the gaps between the larger spheres.

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Four products cover most application needs

All of the new "60 percent dispersions" (see Table 1) are free of organic cosolvents and external emulsifiers. The star among these products is the aliphatic, high-performance dispersion "Impranil DLU". It can be used to formulate particularly high-quality coatings for upholstery, automobile seats, sports goods and other technical products and is characterised by extremely good foamability, flexibility and hydrolytic stability.The "Impranil" high-solids dispersion range includes three other products. "LP RSC 1554" gives textiles more volume and body, and is well suited to mechanical foaming. This dispersion can be used to formulate fashionable and cost-effective coatings for such things as sports goods and interior furnishings. "LP RSC 1380" is used in similar applications to make the textile materials supple, and in particular to improve their haptic properties.

"LP RSC 1537" is a speciality product for the transfer process, in which the top layer is first applied to a transfer paper, which may or may not be grained. This product is extremely well suited to the creation of an adhesion layer, which is subsequently transferred to the textile together with the top layer and is characterised by its extreme softness and flexibility. But like the other representatives of the "60 percent products," this dispersion can also be applied using the direct process to produce soft and waterproof materials.The high-solids dispersions can be used as a compact intermediate coat in a four-coat system to produce high-grade synthetic leather for upholstered furniture and automotive interiors, for example. Such synthetic leathers are extraordinarily scratch and impact-resistant in addition to being resistant to abrasion and hydrolysis.

In addition to these products, the company has developed a new aliphatic polyurethane dispersion for the topcoat. This is similarly free of organic cosolvents and external emulsifiers. The "DLC-F" grade makes the surface of synthetic leathers resistant to abrasion and ageing.

Emissions reduced by a factor of ten

The waterborne PU dispersions can be used to produce synthetic leather and textiles whose resistance to abrasion and hydrolysis is similar to those coated with solventborne PU raw materials (see Table 2). Emissions analyses according to VDA 278, however, show that the new dispersions help lower the VOC and fogging values of the materials by a factor of ten. The same applies to the fogging test according to DIN 75201, in which the quantity of condensable substances is determined (see Figure 2).Emissions from textile materials coated with dispersions from this new range are also lower than those of coatings formulated with waterborne PU dispersions containing cosolvents. Many PU dispersions containing NMP (N-methylpyrrolidone) are still currently on the market.

Application and environmental benefits

This new generation of waterborne products means that the days in which environmentally friendly, waterborne dispersions for the coating of textiles were dismissed as offering poor productivity or inadequate resistance properties can finally be relegated to history. For the production of synthetic leather, the frothed foam process offers ecological advantages over the conventional coagulation process as well as economic advantages over conventional PU dispersions.Synthetic leather producers are currently presenting synthetic materials based on these new high-solids dispersions to brand-name manufacturers of finished goods.

Results at a glance

››› Polyurethane synthetic leathers are normally manufactured in a multi-stage process in which a soft porous layer is produced by removing toxic dimethyl formamide (DMF) from a solventborne layer, then applying a solventborne wear layer.››› By using a bimodal particle size distribution, a range of solvent-free waterborne PU dispersions with a very high solids content of 60% has been produced. The soft layer can be produced by foaming the dispersions with air, and the high solids means that thick layers can be applied in a single step.››› Another solvent-free dispersion is available which provides a top layer with excellent lightfastness and physical resistance properties. The finished materials also offer low fogging (residual emission) levels.

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Physical properties	Impranil DLU Polyether/ polycarbonate-polyurethane	Impranil LP RSC 1537 Polyester-polyurethane Impranil LP RSC 1554	Impranil LP RSC 1554 Polyester-polyurethane	Impranil LP RSC 1380 Polyester-polyurethane
100% modulus [MPa]	2 - 3	1.2	3	1.0
Tensile strength [Mpa]	20 – 30	13	26	14
Elongation at break [%]	600 – 800	1200	1300	1300
Swelling in ethyl acetate [%]	500	120	300	400
Swelling in water [%]	13	10	7	10
Hydrolysis	++	+	0	0
Melting point [°C]	200 – 230	200 - 210	210	215
Shore A hardness	60	55	65	55
Lightfastness	7	7	7	7
Ionic charge	a	a	a	a

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Test	Solventborne	Waterborne
Peel strength (kg/cm)dry	4.0	> 5.0
Peel strength (kg/cm)wet	3.8	> 5.0
Total VOC mg/kg (thermal desorption test)	> 500	< 50
Abrasion resistance Taber 1000 revs/ H22 wheel, 10N weight	28 mg	23mg
Hydrolysis resistance 'Jungle test': 70 °C; 95 % humidity	< 4 weeks	6 weeks

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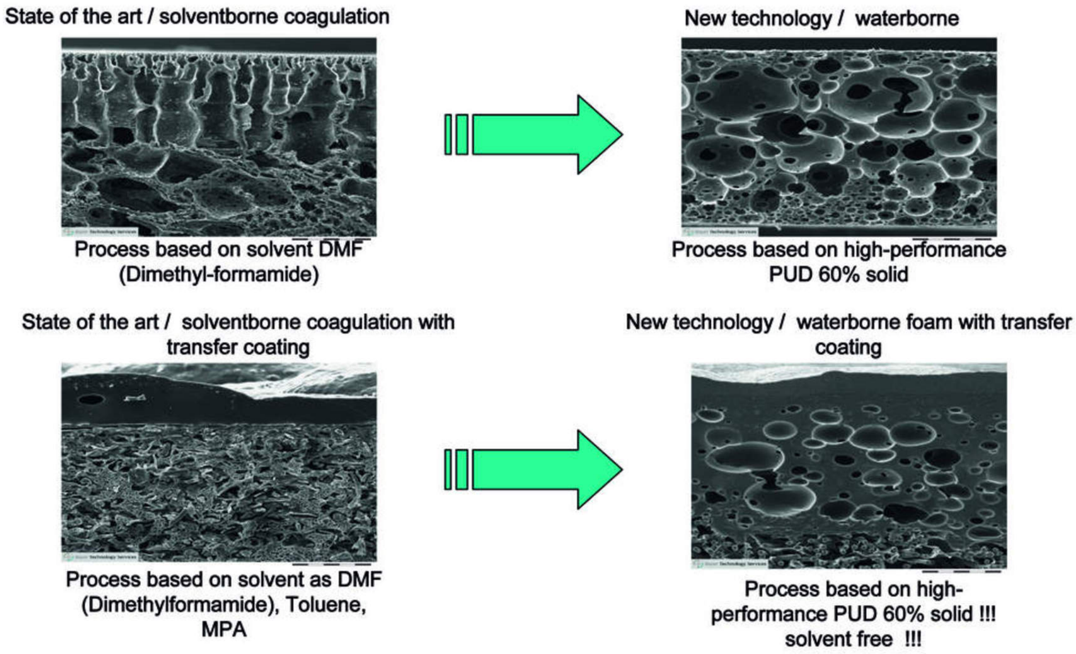

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