

The invention relates to a process for the production of laminated films by adhesive bonding of at least two films by means of a polyurethane adhesive with moistening of the adhesive layer or of the adhesive-free film.

It is known that laminated films, such as, for example, those comprising polyethylene, polypropylene, polyamide, polyethylene terephthalate or cellophane films or aluminium foils, are produced using polyurethane adhesives. These adhesives are one-component systems which are cured by the presence of moisture or two-component systems based on linear polyurethanes and polyisocyanates having a higher functionality as crosslinking agents. By way of example, reference may be made in this context to European Patent No. 0 176 726, German Patent No. 2 549 227 and German Offenlegungsschrift No. 4 021 113.

Laminated films are usually produced using catalyst-free polyurethane systems as adhesives since catalysts for accelerating the curing reduce the pot life to such an extent that practical use is difficult if not impossible. However, the use of catalyst-free polyurethane systems has the disadvantage that very long curing times and low initial strengths result and that marked migration of polyisocyanate in the films occurs, unless these are metal foils.

To reduce the reaction times of polyurethane adhesive, in the case of one-component systems the adhesive layer is moistened, for example by spraying with water, during lamination. This had a certain effect, but one which was still far from satisfactory for use in practice.

The object of the invention was therefore further to improve the known processes for the production of

laminated films and in particular to achieve more rapid curing and higher initial strength as well as lower isocyanate migration without at the same time also reducing the pot life of the polyurethane adhesive.

According to the invention, this object is achieved by a process for the production of laminated films by adhesive bonding of at least two films by means of a polyurethane adhesive with moistening of the adhesive layer or of the adhesive-free films, which is characterized in that the moistening is carried out using an aqueous solution of at least one catalyst which accelerates the curing reaction of the polyurethane adhesive.

Since the aqueous catalyst solution does not come into contact with the polyurethane adhesive until immediately before the lamination of the films, the catalyst has no possibility of influencing the pot life of the polyurethane adhesive. On the other hand, as a result of moistening with an aqueous catalyst solution, the reaction time of the polyurethane adhesive is reduced to such an extent that considerably increased initial strengths of the laminated film and substantially shorter curing times and lower isocyanate migrations are obtained. It is surprising that such a strong effect is achieved, particularly with regard to the initial strengths, although in the process according to the invention the polyurethane adhesive layer initially comes into contact only superficially with the catalyst solution.

The process according to the invention is suitable for the lamination of any films or laminate materials. These may be any desired plastics, such as polyolefins, polyamides, polyesters, polyethers or polyvinyl chloride, metal foils, such as aluminium foils,

sheet-like structures comprising fibres, such as paper or cardboard, or the like. According to the invention, identical or different films of these types may be laminated with one another.

The polyurethane adhesives to be used according to the invention are known from many publications and may be one-component systems or two-component systems. The polyurethane adhesives are composed of at least one organic polyisocyanate and at least one polyol, which in turn may be, for example, an oligourethane having several hydroxyl groups or a polyesterpolyol, polyetherpolyol or polyetheresterpolyol.

Typical examples of diisocyanates for polyurethane adhesives are 1,6-diisocyanatohexane, 1,10-diisocyanatodecane, 1,3-diisocyanatocyclopentane, 1,4-diisocyanatocyclohexane, 1-isocyanato-3,3,5-trimethyl-3- or -5-isocyanatomethylcyclohexane, 4,4'-2,4'- and 2,2'-diisocyanatodiphenylmethane, 1,5-diisocyanatonaphthalene, 4,4'-diisocyanatodicyclohexylmethane, 1,4-diisocyanatobenzene and/or 2,4- or 2,6-diisocyanatotoluene. Suitable polyols are, for example, alkanediols having a linear or branched carbon chain, such as ethylene glycol, 1,2-dihydroxypropane, 1,3-dihydroxypropane, 1,4-dihydroxybutane, 1,6-dihydroxyhexane or neopentylglycol.

The polyurethane adhesives used as one-component systems are usually prepolymers of the polyisocyanates and polyols having free isocyanate groups which effect curing by reaction with water. Examples of these are to be found in German Patent No. 2 549 227. Two-component systems consist either of prepolymers having free isocyanate groups which are cured with the aid of crosslinking agents containing hydroxyl groups, or of prepolymers having free hydroxyl groups which are cured with the aid of crosslinking agents containing isocyanate

groups. Examples of the former are to be found in German Offenlegungsschrift No. 4 021 113 and European Patent No. 0 150 444. Examples of the latter are described in European Patent No. 0 176 726.

Regardless of the group to which the polyurethane adhesives are to be assigned, they may be solvent-containing or solvent-free, in the former case organic solvent being expelled before the adhesive bonding process.

Catalysts which accelerate the curing reactions of the polyurethane adhesive and may therefore be used according to the invention are known as such. If they are water-soluble or substantially water-soluble, they can be used in the present process, it being obvious to a person skilled in the art that he can optimize the desired improvements for certain polyurethane systems by the choice of the catalysts.

Both Lewis bases and Lewis acids may be used as catalysts for the polyurethane adhesive. The most important Lewis bases are tertiary amines having a very wide range of structures, such as diazabicyclooctane, triethylamine, dimethylbenzylamine, bisdimethylaminoethyl ether, tetramethylguanidine or bisdimethylaminoethylphenol. The most important catalytically active Lewis acids are organometallic compounds, in particular organotin compounds, such as tin diethylhexanoate, dibutyltin dilaurate, dibutyltinbisdodecylmercaptide or phenylethyllead dithiocarbamate. Organometallic compounds activate the isocyanate groups in that they increase the electrophilic character, while bases increase in particular the nucleophilic character of the OH groups.

Other known catalysts are alkali metal salts of organic acids and phenols and phenol Mannich bases,

phosphines and phospholine oxides.

Combinations of several catalysts may of course also be used, such as combinations of tertiary amines and organotin compounds, and such combinations may even have synergistic effects. It is furthermore self-evident that the catalysts are also chosen on the basis of aspects such as the intended use of the laminated film. For example, it will not be possible to use lead compounds as catalysts when the laminated film is used in the food sector, which is of particular importance here. Technically important catalysts for polyurethanes, which may also be used in the present invention, are described in "Kunststoffhandbuch" [Plastics Manual], 2nd Edition, Volume 7 (Polyurethanes), from Carl Hanser Verlag Munich, pages 92 to 98, the content of which is referred to here.

In the present process, ϵ -caprolactam proved to be particularly suitable in addition to the known tertiary amines and/or organotin compounds. The catalyst is contained in the aqueous solution according to the invention expediently in a concentration of 0.001 to 10% by weight, preferably in a concentration of 0.01 to 5% by weight and in particular in a concentration of 0.1 to 2% by weight. Within these ranges, variation is possible depending on the catalytic activity of the individual compound for a certain system.

It is particularly preferable to add at least one wetting agent to the aqueous solution used according to the invention, since, surprisingly, a synergistic action occurs as a result of the combined use of catalyst and wetting agent in the moistening solution.

Any desired wetting agents or surfactants, which may be anionic, cationic, nonionic or amphoteric wetting agents, may in principle be used here. Examples of anionic surfactants are alkylbenzenesulphonates,

alkanesulphonates, fatty alcohol sulphates, fatty alcohol ether sulphates, α -olefin sulphonates, α -ester sulphonates, alkyl phosphates and alkyl ether phosphates. Examples of cationic wetting agents are alkylammonium compounds and imidazolinium compounds. Examples of nonionic wetting agents are fatty alcohol ethoxylates, alkylphenol ethoxylates, fatty amine ethoxylates, fatty acid ethoxylates, fatty ester ethoxylates, other alkoxyates, alkanolamides, sugar surfactants and amine oxides. In the present process, the alkanesulphonates, such as, for example, sulphosuccinic esters, have proved expedient.

The aqueous solutions used according to the invention contain the individual wetting agents or surfactants or mixtures of wetting agents expediently in a concentration of 0.001 to 5% by weight, preferably in a concentration of 0.01 to 1% by weight, in particular in a concentration of 0.01 to 0.1% by weight.

In the process according to the invention, the uncured polyurethane adhesive layer is applied to a film by conventional technique, and the coated film is combined with a second adhesive-free film and laminated by press rolls. According to the invention, the aqueous catalyst solution may be applied either anywhere before the pair of laminating rolls to the adhesive layer on one film or to the adhesive-free other film, for example by spraying, wiping or immersion. However, moistening may also be effected by providing, at the feed of the pair of laminating rolls in the region before the combination of the two films, a tank containing the aqueous catalyst solution which moistens the adhesive immediately before combination with the adhesive-free film. In each case in the present process, the aqueous catalyst solution is expediently supplied in excess so that the adhesive layer

is flooded on moistening. This can be effected, for example, by excessive spraying and allowing the excess solution to run off or with the aid of the stated tank at the nip of the laminating rolls.

However the process according to the invention is carried out, the outstanding advantages of rapid initial curing and comparatively rapid final curing and low isocyanate migration decreasing rapidly during curing and surprisingly improved levelling of the adhesive in the roll nip of the pair of laminating rolls are achieved.

The course of this process is illustrated schematically by means of an Example in the drawing.

According to the drawing, a film 1 is fed via a roll 12 to the pair of laminating rolls 10/11 and coated with adhesive with the aid of the applicator roll system 7, 8, 9. The reference numeral 6 denotes an adhesive tank above the roll nip of the rolls 7 and 8. The adhesive layer on the film 1 has the reference numeral 3.

Simultaneously with the film 1, a film 2 without adhesive is fed to the pair of laminating rolls 10, 11. A tank 5 with a solution containing aqueous catalyst and wetting agent is present before the entrance into the roll nip of the pair of laminating rolls 10, 11, with the aid of which solution the adhesive layer 3 on the film 1 is moistened before the two films are combined in the roll nip of the pair of laminating rolls 10, 11. The finished laminated film produced according to the invention leaves the pair of laminating rolls 10, 11 and has the reference numeral 4. The adhesive film on the applicator roll system 7, 8, 9 was denoted by 6a.

Examples

Example 1

In this Example, a standard nylon film was

laminated with a standard polyethylene film by means of a one-component polyurethane adhesive. The adhesive with the trade name Polybond ET 100 X 142 (Morton International GmbH, Bremen) consisted of a commercial prepolymer product having terminal isocyanate groups and obtained from diphenylmethane 4,4'-diisocyanate and polypropylene glycol ether. The adhesive was applied to the nylon film in an amount of about 1.5 g/m², and lamination was carried out under constant conditions of 23°C and 55% relative humidity. The moistening solution was applied to the polyethylene film by spraying on.

For comparative purposes, one experiment was carried out without moistening, in a second experiment spraying was carried out with pure water and in a third experiment spraying was effected with an aqueous solution of 1% of ϵ -caprolactam and in a fourth experiment spraying was effected with an aqueous solution of 1% of ϵ -caprolactam and 0.05% of sodium dihexylsulphosuccinate. The ϵ -caprolactam is a catalyst for curing polyurethane, and the sodium dihexylsulphosuccinate is a wetting agent.

For the four laminated films obtained, the bond strengths were determined similarly to DIN 53 357 in N/15 mm and the isocyanate migration according to BGesundh. Bl. 13, page 262 (1970) and 14, page 13 (1971) in μ m/50 mm (extraction with water, amine determination), said determinations being carried out after certain time intervals. The results are shown in Tables I and II below.

Table I
Bond strengths (N/15 mm)

	Immedi- ately	1 h	After 2 h	4 h
ET 100 x 142	0.08	0.11	0.12	0.14
ET 100 x 142 + H ₂ O	0.09	0.60	1.20	2.50
ET 100 x 142 + H ₂ O + 1% of ε-caprolactam	0.09	1.57	2.10	5.0
ET 100 x 142 + H ₂ O + 1% of ε-caprolactam + 0.05% of sodium dihexylsulpho- succinate	0.08	1.40	2.20	6.0

Table II
Isocyanate migration (μm/50 ml)

	After 2nd day	After 3rd day	After 6th day
ET 100 x 142	73	51	34
ET 100 x 142 + H ₂ O	7.9	5.3	0.5
ET 100 x 142 + H ₂ O + 1% of ε-caprolactam	4.5	1.4	n.n.*
ET 100 x 142 + H ₂ O + 1% of ε-caprolactam + 0.05% of sodium dihexylsulpho- succinate	2.0	0.9	n.n*

*n.n. = Cannot be determined

The results of Table I show that the initial adhesion after one hour was considerably better in the case of the laminated films produced according to the invention than in the case of the other two laminated films. Furthermore, the Table shows that final curing

(5.0 N/15 mm) was practically achieved after only 4 h in the case of the laminated films according to the invention whereas the laminated films outside the inventive concept were by no means completely cured at this time. After 4 h, the strength was so great in the case of the laminated films produced according to the invention that tears occurred in the film rather than separation at the adhesive layer. The values in Table II show that the isocyanate migration in the process according to the invention decreased considerably compared with the use of water alone, and that, in contrast to the laminated films outside the inventive concept, according to the invention isocyanate migration can no longer be detected after 6 days. Surprisingly, the isocyanate migration could be further greatly reduced by adding the wetting agent, while the course of curing was not significantly influenced by the wetting agent.

Example 2

Laminated films were produced using a two-component polyurethane adhesive by the same process as in Example 1. This adhesive consisted of a prepolymer product having terminal isocyanate groups and obtained from diphenylmethane 4,4'-diisocyanate and a polypropylene glycol ether (commercial name PENTACOL SK 400 A from Morton International GmbH, Bremen) and a polypropylene glycol ether (trade name C 78 from Morton International GmbH, Bremen) as a crosslinking agent having terminal hydroxyl groups.

Once again, four laminated films were produced, in a first experiment without moistening solution, in a second experiment by moistening with water alone, in a third experiment with the use of an aqueous catalyst solution and in a fourth experiment with the use of an

aqueous solution of catalyst and wetting agent. The catalyst and wetting agent and their concentration were the same as in Example 1.

The values of the bond strengths and isocyanate migration determined according to Example 1 are shown in Tables III and IV, in the latter case, a comparison being made only with the sample without moistening solution. The results show the same trend as those of Example 1.

Table III

Bond strengths (N/15 mm)

	After 2 h	After 6 h	After 24 h
SK 400 A + C 78 (100:35)	0.03	0.08	3.0
SK 400 A + C 78 (100:35) + H ₂ O	0.05	1.0	4.4
SK 400 A + C 78 (100:35) + H ₂ O + 1% of ϵ -caprolactam	0.06	1.2	6.0
SK 400 A + C 78 (100:35) + H ₂ O + 1% of ϵ -caprolactam + 0.05% of sodium dihexyl- sulphosuccinate	0.10	2.3	7.0

Table IV

Isocyanate migration (μ m/50 ml)

	After	1st day	2nd day	3rd day	5th day	6th day
SK 400 A + C 78 (100:35)	2.8	-	7.2	-	n.n	
SK 400 A + C 78 (100:35) + H ₂ O + 1% of ϵ -caprolactam + 0.05% of sodium dihexylsulphosuccinate	1.1	n.n.				



Patent Claims

1. Process for the production of laminated films by adhesive bonding of at least two films by means of a polyurethane adhesive with moistening of the adhesive layer or of the adhesive-free film, characterized in that moistening is carried out using an aqueous solution of at least one catalyst which accelerates the curing reactions of the polyurethane adhesive.
2. Process according to Claim 1, characterized in that an aqueous solution which contains at least one wetting agent in addition to the catalyst is used for moistening.
3. Process according to Claim 1 or 2, characterized in that a tertiary amine and/or an organometallic compound, preferably an organotin compound, are used as the catalyst.
4. Process according to Claim 1 or 2, characterized in that ϵ -caprolactam is used as the catalyst.
5. Process according to any of Claims 1 to 4, characterized in that an aqueous solution which contains the catalyst in a concentration of 0.001 to 10% by weight, preferably 0.01 to 5% by weight, in particular 0.1 to 2% by weight, is used.
6. Process according to any of Claims 1 to 5, characterized in that an aqueous solution which contains at least one alkanesulphonate, preferably a sulphosuccinate, as a wetting agent is used.
7. Process according to any of Claims 2 to 6, characterized in that an aqueous solution which contains the wetting agent in a concentration of 0.001 to 5% by weight, preferably 0.01 to 1% by weight, in particular 0.01 to 0.1% by weight, is used.
8. Process according to any of Claims 1 to 7,



characterized in that moistening with the aqueous solution is effected by spraying, wiping, immersion or providing a tank of aqueous solution before the point of combination of the films.