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UUSI FTALAATTIVAPAA ISOSYANURAATTIKOOSTUMUS JA SEN KÄYTTÖ

NOVEL PHTHALATE-FREE ISOCYANURATE COMPOSITION AND USE OF SAME

Novel phthalate-free isocyanurate composition and use of same

The present invention relates to the technical field of adhesion promoters, in particular of adhesion promoters for coating compositions based on plasticized PVC, and provides phthalate-free, low-monomer-content, low-viscosity and low-volatility compositions which have excellent suitability as adhesion promoters.

Prior art

It is known that the capability of plasticized PVC to adhere on substrates can be improved by adding to the plasticized PVC an adhesion promoter comprising isocyanate groups. Adhesion capability thus improved is important by way of example when the intention is to produce synthetic textile materials provided with a PVC covering. Adhesion promoters used are preferably isocyanurates which comprise isocyanate groups and which can be produced from diisocyanates by oligomerization, in particular trimerization. Diisocyanates used for this purpose are (TDI) normally mixtures of isomeric diisocyanatotoluenes consisting mainly of 2,4-diisocyanatotoluene (2,4-TDI) and 2,6-diisocyanatotoluene (2,6-TDI), these mixtures being readily available commercially. These can easily be converted almost entirely to isocyanurates comprising isocyanate groups. The almost complete conversion is necessary for reasons of workplace safety and product safety, and EU regulation, and for these reasons the residual content of diisocyanates in the adhesion promoter composition is kept below 0.5% by weight. Less suitable are diisocyanatodiphenylmethanes (MDI), which likewise have good availability, but give poorer trimerization than TDI and therefore can lead to an undesirable high residual content of diisocyanates. MDI-based isocyanurates comprising isocyanate groups moreover exhibit poor solubility and have a tendency towards crystallization.

Isocyanurates comprising isocyanate groups

Isocyanurates comprising isocyanate groups provide easy handling as adhesion promoters especially when they are used in the form of a solution in a plasticizer. TDI-derived isocyanurates comprising isocyanate groups are preferably produced within the plasticizer used as solvent. These adhesion promoters, and adhesion promoter compositions comprising plasticizer, production thereof and use thereof are described by way of example in DE2419016 A1 (GB1455701 A) or in WO2011/095569.

Plasticizer and plasticized PVC

For the purposes of the present invention, plasticizers are typically organic substances which have no volatility or only low volatility and which do not enter into covalent bonding with PVC, but lower its glass transition temperature. Mixing with the plasticizer converts the PVC, which per se is hard and brittle, to a material that is flexible and tough, which the person skilled in the art calls plasticized PVC or flexible PVC. At room temperature, the plasticized PVC is usually a flexible solid. Suitable plasticizers are known to the person skilled in the art. Examples of typical plasticizers are esters of phthalic acid, terephthalic acid, sebacic acid, trimellitic acid, alkanesulphonic acid, citric acid or benzoic acid with alcohols. Quantities of such plasticizers present in plasticized PVC are significant, usually being in the range of 10% by weight to more than 50% by weight of the total mass of the plasticized PVC. Under unfavourable usage conditions, the plasticizer can migrate to the surface or into adjacent materials. The use of plasticized PVC therefore brings the risk of contamination of people and environment by the plasticizer. In the light of these problems, the plasticizers used have in recent years been subject to increasing demands that they cause no harm to humans and are not bioaccumulative.

Short-chain phthalates as plasticizers

The REACH regulation applicable in the European Union places the plasticizers di(2-ethylhexyl) phthalate, dibutyl phthalate and benzyl butyl phthalate on the SVHC (Substances of Very High Concern) list. Furthermore, the plasticizers diisononyl phthalate, diisodecyl phthalate and di-n-octyl phthalate can no longer be used in toys or baby items that children could place in their mouths. In view of these restrictions, which some consumers could regard as unclear and worrying, many producers are generally moving towards avoidance of all phthalate-containing plasticizers and their isomers in the production of plasticized PVC. There is accordingly a demand for phthalate-free plasticizers which achieve the performance level of phthalate-based plasticizers in respect of processability and usage properties.

Phthalate-free plasticizers

In the context of the present invention, the expression “phthalate-free plasticizers” is used for plasticizers comprising – based on the content of plasticizer – less than 1.0% by weight, preferably less than 0.5% by weight, particularly preferably less than 0.1% by weight and particularly preferably 0% by weight, of dialkyl phthalates.

Phthalate-free adhesion promoter compositions

Avoidance of phthalate-containing plasticizers is now also required of adhesion promoter compositions which comprise plasticizers, in particular for sensitive applications involving, for example, skin contact. There is therefore high demand for adhesion promoter compositions which comprise no phthalates but which nevertheless have the good adhesion properties of phthalate-containing adhesion promoter compositions from the prior art. In the context of the present invention, the expression “phthalate-free adhesion promoter compositions” is used for adhesion promoter compositions which – based on their total mass – comprise less than 1.0% by weight, preferably less than 0.5% by weight, particularly preferably less than 0.1% by weight and particularly preferably 0% by weight, of dialkyl phthalates.

A further requirement is that the adhesion promoter compositions are clear, colourless and free from solids or precipitates, do not comprise any highly volatile constituents, i.e. organic compounds with a boiling point of 0°C to 100°C, and, for good processability, have a viscosity at 23°C that is below 30 000 mPas, preferably below 10 000 mPas and particularly preferably below 5000 mPas. The residual content of monomeric diisocyanates should be below 0.8% by weight, preferably below 0.6% by weight and particularly preferably not more than 0.5% by weight. No combination of all of these product properties has hitherto been described in the prior art.

By way of example, the adhesion promoter compositions described in WO 2005 70984 A1, based on diisononyl phthalate, are not very suitable for sensitive applications. DE 2551634 A1 and EP 1378529 A1 postulate that TDI-based isocyanurates which comprise isocyanate groups and are suitable as adhesion promoters can be produced in arbitrarily selective solvents, among which are also phthalate-free plasticizers. However, this is not true in practice. Experiments carried out by the inventors revealed that arbitrarily selected phthalate-free plasticizers certainly do not lead to adhesion promoter compositions that comply with all of the requirements described. This is also true for the plasticizers described in DE 102007034977, which are based on alkanesulphonic esters of phenol (ASE) and are marketed with the trademark Mesamoll®. DE 3041732 A1 describes, as adhesion promoters, suitable solutions of isocyanurates which comprise isocyanate groups but which are produced from MDI. These solutions are unsuitable for the abovementioned reasons.

Object of the invention

It was therefore an object of the present invention to provide, as adhesion promoters, suitable compositions of isocyanurates comprising isocyanate groups, which, although comprising phthalate-free plasticizers, achieve the level of the phthalate-containing adhesion promoters from WO2005/70984 A1 in respect of their mechanical properties, e.g. bond strengths. The isocyanurates comprising isocyanate groups are to be based on isomer mixtures of TDI that are available on a large industrial scale. The compositions are to be clear and almost colourless, their viscosity at 23°C is to be < 30 000 mPas, preferably below 10 000 mPas and particularly preferably below 5000 mPas, and the content of free TDI (all isomers) is to be below 0.8% by weight, preferably below 0.6% by weight and particularly preferably not more than 0.5% by weight. The volatility of the plasticizer used should be no higher than that of isononyl benzoate.

Volatility of the plasticizer

The volatility of the plasticizer used should not be less favourable than that of isononyl benzoate (INB). INB is accepted worldwide in relation to volatility as a carrier for isocyanurate in its capacity as active substance in adhesion promoter. However, higher volatility is undesirable. The volatility of a substance is determined here by thermogravimetric analysis (TGA).

Achievement of the object

The object is achieved by, and the present invention therefore provides, compositions comprising:

a) isocyanurates comprising isocyanate groups and
b) benzyl alkyl adipate,

where the ratio by weight of a) to b) is in the range of 1:1 to 1:8, preferably of 1:1.2 to 1:4 and particularly preferably of 1:1.5 to 1:2.5.

In a preferred embodiment, the benzyl alkyl adipate bears, as alkyl group, a branched or unbranched C_6 to C_{16} alkyl group, preferably an unbranched or branched octyl group and most preferably an isooctyl group.

Very particular preference is given to the use of benzyl octyl adipate as component b).

In a preferred embodiment of the invention, the compositions comprise 20% to 35% by weight of isocyanurates comprising isocyanate groups and 80% to 65% by weight of benzyl octyl adipate.

In another preferred embodiment, the compositions comprise, based on the total mass of the composition, up to 50% by weight, preferably 0.1% to 40% by weight, of a diluent. This is preferably a diluent from the group comprising alkyl acetate, preferably butyl acetate, ethyl acetate, propyl acetate, N-alkylpyrrolidone, N-octylpyrrolidone, N-decylpyrrolidone, DMF, acetone, alkyl benzoates, with preference benzyl benzoate, paraffins, white oils, and low-aromatic-content aliphatics, and mixtures of these substances.

Isocyanurates which comprise isocyanate groups and which can be used advantageously as component a) are obtainable by trimerization of a mixture of isomeric diisocyanatotoluenes comprising 2,4-diisocyanatotoluene and 2,6-diisocyanatotoluene.

Isocyanurates which comprise isocyanate groups and which are preferably used as component a) are obtainable by trimerization of a mixture of 65% to 95% by weight of 2,4-diisocyanatotoluene and 5% to 35% by weight of 2,6-diisocyanatotoluene, where the percentages by weight are respectively based on the total quantity of diisocyanatotoluenes.

The production of component a) can be achieved by trimerization of the diisocyanate mixtures by known processes of the type described by way of example in WO 2005 70984 A1.

The trimerization is preferably carried out in the presence of plasticizer component b).

The present invention also provides a process for the production of the compositions of the invention, in which diisocyanates are trimerized in the presence of the benzyl alkyl adipate b) to give the isocyanurates a) comprising isocyanate groups.

The trimerization reaction typically takes place in the temperature range of 40 to 140°C, preferably 40 to 80°C. The trimerization is terminated when the content of monomeric diisocyanates in the reaction mixture is 0.8% by weight, preferably 0.6% by weight, and particularly preferably 0.5% by weight or less.

The above termination can be achieved by complete or partial deactivation of the catalyst, for example by thermal decomposition of the catalyst or addition of a reaction terminator. Protic acids, acyl chlorides or methylating compounds can be used as reaction terminators. It is particularly preferable to use alkyl phosphates, in particular dibutyl phosphate, or methyl toluenesulphonate. When a reaction terminator is used, the quantity used thereof is typically 0.22% to 4% by weight, preferably 0.1% to 2% by weight, particularly preferably 0.2% to 1% by weight, based on the total quantity of diisocyanates used. The product then typically comprises 3% to 7% by weight of isocyanate groups, preferably 4.5% to 6%.

In a preferred embodiment, diisocyanates used in the process of the invention are diisocyanatotoluenes, particularly preferably mixtures consisting essentially of 2,4-TDI and 2,6-TDI that are available on a large industrial scale. The mixtures are mixtures of isomeric diisocyanatotoluenes comprising 65% to 95% by weight of 2,4-diisocyanatotoluene and 5% to 35% by weight of 2,6-diisocyanatotoluene and are produced with catalysis. The TDI isomer mixtures particularly preferably comprise 75% to 85% by weight of 2,4-TDI in a mixture with 15% to 25% by weight of 2,6-TDI. An example of these TDI isomer mixtures that are particularly preferably to be used is the product Desmodur® T80, obtainable commercially from Covestro AG.

Production of component a) can use a catalyst which serves for the initiation and acceleration of the trimerization reaction and which also, at relatively high temperatures, leads to selective incorporation of TDI. These catalysts have phenolic OH groups and N,N-dialkylaminomethyl groups attached to aromatic systems (alkyl: C1-C3 alkyl chain and/or alkylene chain having 1 to 18 carbon atoms optionally separated by oxygen or by sulphur).

These groups can be distributed over a plurality of molecules or positioned on one or more aromatic rings. Compounds used as catalyst systems are preferably those that comprise not only hydroxy but also aminomethyl groups in a molecule.

It is particularly preferable to use systems in which C1-C3 dialkylaminomethyl groups are positioned ortho to aromatic hydroxy groups.

The synthesis of Mannich bases suitable as catalysts is described by way of example in DE 25 51 634 A1 and WO 2005 70984 A1. Mannich bases to be used with preference are those based on phenyl, p-isononylphenol or bisphenol A, these being obtained by reaction with dimethylamine and formaldehyde, for example according to DE-A 2 452 531 or Synth. Commun. (1986), 16, 1401-9. In particular, preference is given to Mannich bases based on phenol or bisphenol A.

The catalysts to be used are used as pure substance or in solution, preferably in a plurality of small portions or continuously.

The compositions of the invention are clear, colourless or almost colourless liquids which have surprising stability in storage, and even after storage for several weeks have no tendency towards discoloration or crystallization or towards formation of precipitates or phase separation. Before and after storage they moreover feature extremely low content of free TDI (i.e. monomeric diisocyanatotoluenes) – a particular advantage of the compositions of the invention because of the relatively low boiling point of this toxicologically questionable diisocyanate.

Comparative Examples 1 to 6 set out below therefore not only reveal that the object underlying this invention cannot be achieved with arbitrarily selected phthalate-free plasticizers but moreover prove that the present invention also provides a process that can advantageously produce the combination of plasticizer and isocyanurates comprising isocyanate groups which, in the form of adhesion promoter compositions, provides the required properties.

Use of the compositions of the invention

The compositions of the invention are suitable as adhesion promoters, particularly for coatings made of plasticized PVC, or as adhesion-promoting additions for PVC plastisols. The person skilled in the art understands the expression “PVC plastisols” to mean liquid dispersions of PVC in a plasticizer which gel for example through heating to a relatively high temperature and therefore can be used for the production of plasticized PVC. The compositions of the invention can be used particularly advantageously as adhesion promoters between substrates made of synthetic fibres having groups reactive towards isocyanate groups, e.g. polyamide or polyester fibres, and PVC plastisols or flexible-PVC melts. It is self-evident that the solutions of the invention can also be used to improve the adhesion of plasticized PVC on areal substrates, for example on foils.

The compositions of the invention are therefore particularly suitable as adhesion promoters for coating compositions based on plasticized PVC. For the purposes of the present invention, the expression “coating compositions based on plasticized PVC” encompasses not only coating compositions comprising plastisols but also coating compositions which, when applied to the substrate, take the form of compositions comprising molten flexible PVC; the former are preferred here.

Particularly suitable as substrates to be coated are textiles such as woven fabrics made of natural fibres, of synthetic fibres, or of glass fibres. Particularly suitable synthetic fibres are polyamides and polyester fibres. Leather can moreover be used as substrate.

The compositions of the invention can be used for the production of substrates with coatings comprising, or consisting of, plasticized PVC. If the coating does not consist of plasticized PVC, it typically comprises at least 50% by weight of the same, preferably at least 75% by weight and particularly preferably 90% by weight to 99% by weight, alongside additional substances regarded by the person skilled in the art as customary for PVC coatings. The compositions of the invention can by way of example be applied here to the substrates to be coated by printing, doctor-system methods, screening or spraying, or by immersion. As required by the product to be produced, one or more adhesion-promoter-free PVC layers is/are then applied, for example in the form of plastisols or by extrusion coating or hot-melt roll coating, or by lamination, to the substrate surfaces thus treated. The compositions of the invention can also particularly preferably be added to a PVC plastisol before it is applied.

Quantities are used on the compositions of the invention are usually such that, based on plasticizer-free PVC of the coating composition, 0.5% to 40% by weight, preferably 2% to 15% by weight, of isocyanurates comprising isocyanate groups are present. However, the solutions of the invention can also be used in any other desired quantities appropriate to the respective application sector.

Irrespective of the application method used, the production of the finished layers, i.e. the reaction of the isocyanate groups of the adhesion promoter with the substrate and the gelling of the PVC layer, is achieved in conventional manner at relatively high temperatures; temperatures used here are between 110 and 210°C, depending on the composition of the PVC layers.

The present invention also provides coatings and coated substrates for textiles or woven fabrics, these being obtainable by using the adhesion promoter compositions described above. The compositions of the invention are suitable as adhesion promoters for coating compositions based on plasticized PVC, and therefore for the production of coatings comprising, or consisting of, plasticized PVC, i.e. in particular for the production of tarpaulins, billboards, air-supported structures and other textile structures, flexible containers, tent roofs, awnings, protective apparel, conveyor belts, flock carpets or foamed synthetic leather.

The compositions of the invention have particularly good suitability as adhesion-promoting additives for the coating of substrates having groups reactive towards isocyanate groups, in particular for coating of yarns, mats and woven fabrics made of polyester fibres or of polyamide fibres.

Inventive Example and Comparative Examples

Unless otherwise noted, all parts and percentages are based on weight.

Determination of parameters

Parameters determined for the products were viscosity at 23°C (VT550 rotational viscometer from Haake GmbH, Karlsruhe) and content of free TDI (gas chromatography, Hewlett Packard 5890 in accordance with DIN ISO 55956). Isocyanate content was determined in accordance with EN ISO 11909. A Mettler Toledo TGA/DSC 3+ SF/1100/189, T = RT to 400°C, 10°C/min, N_2, was used to produce the TGA curves.

Starting materials for Inventive Example and Comparative Examples

Desmodur® T80: TDI isomer mixture consisting of 80% by weight of 2,4-TDI and 20% by weight of 2,6-TDI, Covestro AG.

Vestinol® 9 DINP: Diisononyl phthalate, Evonik.

Adimoll® DB: Dibutyl adipate, Lanxess Deutschland GmbH.

Adimoll® DO: Dioctyl adipate, Lanxess Deutschland GmbH.

Adimoll® BO: Benzyl octyl adipate, Lanxess Deutschland GmbH.

Benzoflex® 2088: Mixture of diethylene glycol dibenzoate, triethylene glycol dibenzoate and dipropylene glycol dibenzoate, Velsicol Chemical Corp.

Mesamoll® II: Phenyl alkanesulphonate, Lanxess Deutschland GmbH.

Catalyst: DABCO TMR 30 (2,4,6-tris(dimethylaminoethyl)phenol)

Reaction terminator: Dibutyl phosphate

TGA:

Plasticizer	Abbreviation	Approximate residual level at 180°C	Approximate residual level at 200°C
Dibutyl adipate	DBA	31	1
Isononyl benzoate	INB	88	70
Benzyl octyl adipate	BOA	96	85
Dioctyl adipate	DOA	98	94
Diisononyl adipate	DINA	100	98
Diisononyl phthalate	DINP	100	100

Table 1: Determination of volatility of various adipates in comparison with the plasticizers INB and DINP by TGA

Table 1 shows that at the usual processing temperatures for PVC plastisols dibutyl adipate (DBA) has already very substantially evaporated. This is unacceptable for reasons of environmental protection and workplace safety. Blistering can moreover occur in the PVC layer; this is likewise extremely unwelcome.

Comparative Example 1 (non-inventive) DINP

180 parts by weight of Desmodur® T80 were trimerized at 55°C in 378 parts by weight of Vestinol® 9 DINP with 1.6 parts by weight of catalyst. The reaction was terminated after 72 hours by adding 2.6 parts by weight of reaction terminator and stirring was continued at 60 to 70°C for three hours. A clear colourless solution was obtained with 5.53% by weight isocyanate content, viscosity at 23°C of 41 400 mPas and 0.14% by weight content of free TDI.

Comparative Example 2 (non-inventive) DBA

The volatility of dibutyl adipate was first determined by TGA (see Table 1).

It was found here that the material underwent almost complete evaporation at the usual PVC-processing temperatures of 180-210°C. This can lead to blistering at the PVC layer and is therefore extremely unwelcome. No further testing was therefore carried out.

Comparative Example 3 (non-inventive) Ethylene glycol dibenzoate and propylene glycol dibenzoate

180 parts by weight of Desmodur® T80 were trimerized at 50°C in 415 parts by weight of Benzoflex® 2088 with 0.7 parts by weight of catalyst. The reaction was terminated after 84 hours by adding 1.7 parts by weight of reaction terminator and stirring was continued at 60 to 70°C for three hours. A clear colourless solution was obtained with 4.8% by weight isocyanate content, viscosity at 23°C of > 200 000 mPas and 1.09% by weight content of free TDI.

Comparative Example 4 (non-inventive) 2.9 parts of Mesamoll® II catalyst

180 parts by weight of Desmodur® T80 were trimerized at 55°C in 504 parts by weight of Mesamoll® II with 2.9 parts by weight of catalyst. The reaction was terminated after 72 hours by adding 4.7 parts by weight of reaction terminator, and stirring was continued at 60 to 70°C for three hours. A clear yellowish solution

was obtained with 4.8% by weight isocyanate content, viscosity at 23°C of 11 600 mPas and 0.25% by weight content of free TDI.

Comparative Example 5 (non-inventive) 1.5 parts of Mesamoll® II catalyst

180 parts by weight of Desmodur® T80 were trimerized at 55°C in 378 parts by weight of Mesamoll® II with 1.5 parts by weight of catalyst. The reaction was terminated after 72 hours by adding 2.6 parts by weight of reaction terminator, and stirring was continued at 60 to 70°C for three hours. A clear yellowish solution was obtained with 5.31% by weight isocyanate content, viscosity at 23°C of > 300 000 mPas and 0.15% by weight content of free TDI.

Comparative Example 6 (non-inventive) Dioctyl adipate

180 parts by weight of Desmodur® T80 were trimerized at 70°C in 534 parts by weight of Adimoll DO with 2.5 parts by weight of catalyst. The reaction was terminated after 5 hours by adding 5 parts by weight of reaction terminator and stirring was continued at 60 to 70°C for 1 hour. No clear solution was obtained. A precipitate formed after a short time. The product cannot therefore be used, and was not analysed further.

Comparative Example 1 corresponds to Example 2 from EP 1 711 546 A1, and serves to permit comparison of the properties of the adhesion promoter compositions of the invention with the prior art. Comparative Examples 4 and 5 demonstrate that increasing the quantity of catalyst does not automatically lead to a product of the invention.

As the non-inventive Comparative Examples 1 to 6 moreover reveal, the selection of the plasticizer has a decisive effect on the result of the trimerization. Use of the phthalate-free plasticizers described in the prior art cannot therefore achieve the desired property combination, or can achieve this only if the TDI trimer concentration does not exceed about 27% by weight. The adhesion promoters either cannot be processed further because of their high viscosity or provide inadequate bond strengths because their TDI trimer concentration is too low.

Inventive Example 1 Benzyl octyl adipate (= -K93)

180 parts by weight of Desmodur® T80 were trimerized at 70°C in 414 parts by weight of Adimoll® BO with 1.6 parts by weight of catalyst. The reaction was terminated after 12 hours by adding 3.2 parts by weight of reaction terminator, and stirring was continued at 60 to 70°C for 1 hour. A clear colourless solution was obtained with 5.3% by weight isocyanate content, viscosity at 23°C of 1924 mPas and 0.5% by weight content of free TDI.

Performance testing and test results:

A PVC-plastisol/adhesion-promoter coating was provided to woven polyester fabric in a test system simulating industrial conditions. The bond strength of this coating was then determined on a standardized test strip. For this, a doctor system was used to coat woven polyester fabric with an adhesive coating comprising adhesion promoter. These coatings were gelled in an oven and then subjected to testing. In the testing for bond strength, two test strips were laid on top of one another (PVC side on PVC side), pressed at low pressure and 180°C, and tested in a tensile tester.

Test equipment:

Balance: Accuracy min. 0.1 g
Stirrer: High-speed stirrer shaft
Mathis Labcoater oven from Mathis AG Zürich
Ametec LR5 K plus tensile tester
Woven polyester fabric: Polyester 1100 dtex L 9/9 Z 60 standard woven fabric

Woven fabric samples measuring about 40 × 25 cm were used for the test.

Composition of PVC plastisol:

70 parts PVC; Vestolit® B 7021 Ultra paste PVC; Vestolit GmbH; Marl
30 parts PVC Vestolit® E 7031 paste PVC; Vestolit GmbH; Marl
33 parts Mesamoll® ASEP plasticizer; Lanxess Deutschland GmbH
33 parts Vestinol® 9 DINP plasticizer; Evonik Oxeno GmbH, Marl
10 parts Durcal® 5 chalk; Omya GmbH; Köln
2.5 parts Baerostab® UBZ 780 RF stabilizer; Baerlocher GmbH; Berlin
1.5 parts Kronos ® 2220 titanium dioxide; Kronos Titan GmbH; Leverkusen

Test specimens:

Adhesive coat	approximately 140 g/m²	140°C/2 min

The test specimens were pressed and bonded after coating and pregelling at 140°C for 2 min at 180°C.

Dimensions: 5 cm width x 25 cm length in weft direction

Testing with Ametec LR5 K plus tensile tester

For production of the PVC plastisol, the starting materials listed above under “Composition of PVC plastisol” were mixed under reduced pressure in a mixer from Drais by stirring for 2.5 hours at maximum rotation rate with water cooling.

Tensile testing:

These samples were then used to determine the bond strengths in a Lloyd M 5 K tensile tester. The bond strength values obtained indicate the force in newtons required to peel 5 cm of the coating from the woven carrier fabric (peel test, presented in the Table as strength in N/5 cm). The values stated in the table were obtained by averaging at least three individual measurements.

Comparative Examples and Inventive Example

As revealed by the measurement results of Inventive Example 1, when the phthalate-free composition of the invention is used as adhesion promoter it provides bond strength values higher than those achieved with the phthalate-containing composition of the prior art (Comparative Example 1). The adhesion promoters from Comparative Examples 3, 5 and 6 were unsuitable for further processing because they either had excessive viscosity or led to precipitates. The compositions of Comparative Examples 4 and 5 moreover had a disadvantageous yellow colouring. Another unexpected finding was that among the adipate class of substances it was only the benzyl octyl adipate of the invention that exhibited unexpectedly good efficacy; the two other products from this substance class either exhibited precipitates or were much too volatile.

Test results:

Example	**Volatility of plasticizer**	**Viscosity**	**Strength of adhesion N/5 cm**
Comparative Example 1 DINP	low	41 000 mPas	156
Comparative Example 2 DBA	too high	not tested	not tested
Comparative Example 3 Benzoflex® 2088	sufficiently low	> 200 000 mPas	could not be tested
Comparative Example 4 2.9 parts of Mesamoll® II catalyst	low	11 600 mPas	148
Comparative Example 5 1.5 parts of Mesamoll® II catalyst	low	> 300 000 mPas	could not be tested
Comparative Example 6 Dioctyl adipate	sufficiently low	precipitated	not tested

Example	**Volatility of plasticizer**	**Viscosity**	**Strength of adhesion N/5 cm**
Inventive Example 1 Benzyl octyl adipate	sufficiently low	1900 mPas	206

PATENTTIVAATIMUKSET

1. Koostumukset, jotka käsittävät:

a) isosyanuraatteja, jotka käsittävät isosyanaattiryhmiä, ja

b) bentsyylialkyyliadipaattia,

jossa a):n painosuhde b):hen on välillä 1:1 - 1:8, edullisesti välillä 1:1,2 - 1:4 ja erityisen edullisesti välillä 1:1,5 - 1:2,5.

2. Patenttivaatimuksen 1 mukaiset koostumukset, jossa bentsyylialkyyliadipaatissa on alkyyliryhmänä haarautunut tai haarautumaton C_6-C_{16}-alkyyliryhmä, edullisesti haarautumaton tai haarautunut oktyyliryhmä, edullisimmin iso-oktyyliryhmä.

3. Patenttivaatimuksen 1 tai 2 mukaiset koostumukset, jossa isosyanaattiryhmiä käsittävät isosyanuraatit ovat saatavissa trimerisoimalla isomeeristen di-isosyanatotolueenien seos, joka käsittää 2,4-di-isosyanatotolueenia ja 2,6-di-isosyanatotolueenia.

4. Yhden tai useamman patenttivaatimuksista 1 - 3 mukaiset koostumukset, jossa isosyanaattiryhmiä käsittävät isosyanuraatit ovat saatavissa trimerisoimalla seos, jossa on 65 - 95 painoprosenttia 2,4-di-isosyanatotolueenia ja 5 - 35 painoprosenttia 2,6-di-isosyanatotolueenia, jossa painoprosentteina esitetyt prosenttiosuudet perustuvat vastaavasti di-isosyanatotolueenien kokonaismäärään.

5. Yhden tai useamman patenttivaatimuksista 1 - 4 mukaiset koostumukset, jotka käsittävät koostumuksen kokonaismassan perusteella enintään 50 painoprosenttia laimenninta, edullisesti laimenninta, joka on valittu alkyyliasetaatin, edullisesti butyyliasetaatin, etyyliasetaatin, propyyliasetaatin, N-alkyylipyrrolidonin, N-oktyylipyrrolidonin, N-dekyylipyrrolidonin, DMF:n, asetonin, alkyylibentsoaattien, mieluiten bentsyylibentsoaatin, parafiinien, valkoisten öljyjen ja matala-aromaattisten alifaattisten aineiden, ja näiden aineiden seosten joukosta.

6. Yhden tai useamman patenttivaatimuksista 1 - 5 mukaisten koostumusten käyttö pehmitettyyn polyvinyylikloridiin perustuvien pinnoitekoostumusten tartuntaa lisäävinä aineina.

7. Patenttivaatimuksen 6 mukainen käyttö, jossa pinnoitekoostumus käsittää ainakin yhtä PVC-plastisolia.

8. Patenttivaatimuksen 5 tai 6 mukainen käyttö alusrakenteiden tuottamiseksi, joiden pinnoitteet käsittävät pehmitettyä polyvinyylikloridia tai koostuvat siitä.

9. Patenttivaatimuksen 8 mukainen käyttö, jossa pinnoitetut alusrakenteet ovat suojapeitteitä, mainostauluja, kuplahalleja ja muita tekstiilirakenteita, joustavia säiliöitä, teltan kattoja, markiiseja, suojavaatteita, kuljetinhihnoja, flokkimattoja tai vaahdotettua synteettistä nahkaa.

10. Yhden tai useamman patenttivaatimuksista 8 ja 9 mukainen käyttö, jossa alusrakenteet ovat tekstiilejä, kudottuja kankaita tai nahkaa.

11. Patenttivaatimuksen 10 mukainen käyttö, jossa kudotut kankaat ovat kudottuja polyesterikankaita tai kudottuja polyamidikankaita.

12. Menetelmä yhden tai useamman patenttivaatimuksista 1 - 5 mukaisten koostumusten tuottamiseksi, jossa di-isosyanaatit trimerisoidaan bentsyylialkyyliadipaatin b) läsnä ollessa isosyanaattiryhmiä käsittävien isosyanuraattien a) saamiseksi.

13. Patenttivaatimuksen 12 mukainen menetelmä, jossa trimerisaatio suoritetaan lämpötila-alueella, joka on 40 - 140 °C, ja lopetetaan, kun reaktioseoksessa käytettyjen di-isosyanaattien pitoisuus on 0,8 painoprosenttia, edullisesti 0,6 painoprosenttia ja erityisen edullisesti 0,5 painoprosenttia tai pienempi.

14. Patenttivaatimuksen 12 tai 13 mukainen menetelmä, jossa käytetyt di-isosyanaatit ovat

isomeeristen di-isosyanatotolueenien seos, joka käsittää 2,4-di-isosyanatotolueenia ja 2,6-di-isosyanatotolueenia.

15. Pinnoitekoostumus, joka käsittää yhden tai useamman patenttivaatimuksista 1 - 5 mukaista koostumusta ja ainakin yhtä PVC-plastisolia.