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(54) **CLEANING COMPOSITION FOR REACTIVE ADHESIVES AND USE THEREOF FOR CLEANING PRODUCTION OF APPLICATION DEVICES**

(57) The invention relates to a composition for use in removing reactive adhesives from production, processing and application devices. The composition comprises at least one thermoplastic polymer that is solid at 25 °C and at least one hindered amine of polyalkyl-

piperidine type. The invention is also related to a method for removing reactive adhesives from production, processing and application devices and to the use of the composition for removing reactive adhesives from production, processing and application devices.

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Description**Technical field**

5 **[0001]** The invention relates to a cleaning composition for removing reactive adhesives from production, processing and application devices.

Background of the invention

10 **[0002]** During processing of reactive adhesives, such as reactive hot-melt adhesives, hardened adhesive particles tend to deposit over time on the surfaces of the equipment. Hardened deposits are formed especially during short term production interruptions and longer stand-stills over night or over weekend. During the non-operation periods, the adhesive composition remains motionless in the equipment and deposits can occur especially on moving parts and nozzles of the processing plant. During production of moisture curable hot-melt adhesives, the hardened deposits are formed
15 in places, where the adhesive comes in contact with the air and moisture of the surroundings. A regular cleaning of the equipment is, therefore, required to prevent unscheduled production interruptions and quality inconsistencies. The equipment must usually also be cleaned between product changes in case the same equipment is used for producing different type of adhesives the contents of which cannot be mixed.

20 **[0003]** The reactive adhesive production plants and application devices such as coating devices have numerous narrow areas such as slots, nozzles, hoses and pipes as well as moving parts such as worms, vanes, rolls and agitators. These can be manually cleaned but only with great cost and labor expense since the cleaning requires at least partial dismantling of the apparatuses.

[0004] There is a need to provide an alternative for the manual cleaning of the processing equipment.

25 **[0005]** Two techniques are commonly used for cleaning reactive adhesive production equipment. The reactive adhesive composition can be removed from the processing apparatus by supplanting with a cleaning composition, which typically contains similar thermoplastic components as reactive adhesive. The cleaning composition has typically a higher viscosity than the reactive adhesive and, therefore, it is able to drag the adhesive with it while flowing through the processing apparatus. An alternative cleaning technique is based on the use of plasticizers, which decrease the viscosity of the reactive adhesive to such extent that it can be readily removed from the equipment surfaces by flushing with a cleaning
30 liquid.

[0006] Both aforementioned cleaning techniques have some disadvantages, which make them somewhat unsuitable for cleaning production and application devices for reactive adhesives, in particular moisture curable adhesives. Supplanting the reactive adhesive is especially difficult in case the device contains dead volumes, which are difficult to flush with the cleaning composition. On the other hand, in case of insufficient cleaning time, part of the moisture curable
35 adhesive remains in the processing apparatus and hardens upon contact with moisture to form deposits of adhesive particles inside the equipment. Such deposits are difficult to detect without dismantling the equipment and the inadequacy of the cleaning time may remain unnoticed for long time periods. The use of plasticizers, especially phthalate based plasticizers, is generally not favored due to environmental and working safety considerations. Furthermore, the plasticizer residues are difficult to remove completely from the equipment and they can contaminate the batches of reactive adhesives produced long after the cleaning of the apparatus. Plasticizer based cleaning liquids are mainly used to clean
40 processing equipment of non-reactive adhesives. Deposits of cured adhesive can only be removed from the equipment surfaces with solutions, which cause the swelling of the cured adhesive.

[0007] There is thus need for an improved cleaning composition and method for removing reactive adhesives from production plants and application devices.
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Summary of the invention

[0008] The object of the present invention is to provide an improved cleaning composition, which enables effective removal reactive adhesives, in particular moisture curable adhesives from production, processing and application de-
50 vices.

[0009] A still further objective is to provide an improved method for removing reactive adhesives, in particular moisture curable adhesives, from production, processing and application devices.

[0010] It was surprisingly found out that a composition containing a carrier based on thermoplastic polymer and at least one hindered amine of polyalkylpiperidine type having a pK_b value of not more than 7.0 is able to solve the problems related to State-of-the-Art cleaning compositions.
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[0011] The subject of the present invention is a composition for use in removing a reactive adhesive from production, processing and application devices as defined in claim 1.

[0012] One of the advantages of the cleaning composition of the present invention is that once it is used for supplanting

reactive adhesive residues from the processing or application equipment, it simultaneously deactivates the reactive adhesive in such extent that formation hardened adhesive deposits upon curing is inhibited. The deactivation effect is based on certain components of the composition, which inhibit the curing reaction of the adhesive. Owing to the inhibition of the curing reaction, the cleaning times can be shortened since it is not necessary to remove the entire reactive adhesive composition from the equipment and still obtain satisfactory cleaning result.

[0013] Another subject of the present invention is a method of removing reactive adhesives from production, processing and application devices.

[0014] Still another subject of the present invention is a use of the cleaning composition of the present invention for removing reactive adhesives from production, processing and application devices.

Detailed description of the invention

[0015] The subject of the present invention is a composition for use in removing a reactive adhesive from production, processing and application devices, the composition comprising:

- a) at least one thermoplastic polymer that is solid at 25 °C and
- b) at least one hindered amine of polyalkylpiperidine type having a pK_b value of not more than 7.0, preferably in the range from 4.0 to 6.5.

[0016] In this document, the term "reactive adhesive" refers to adhesive compositions which develop bonding properties as a result of curing or some other form of reaction mechanism. In case of multi-component adhesives, the reaction can be initiated by mixing of the components. In case of one-component adhesives, the reaction is initiated by applying external energy, such as heat or radiation to the adhesive or by contacting the adhesive with moisture or water.

[0017] In this document, substance names beginning with "poly" designate substances which formally contain, per molecule, two or more of the functional groups occurring in their names. For instance, a polyol refers to a compound having at least two hydroxyl groups. A polyether refers to a compound having at least two ether groups.

[0018] In this document, the term " α -olefin" refers to an alkene having the molecular formula C_xH_{2x} (x corresponds to the number of carbon atoms), which features a double carbon-carbon bond at the first carbon atom (α -carbon). Examples of α -olefins are ethylene, propylene, 1-butene, 2-methyl-1-propene (isobutylene), 1-pentene, 1-hexene, 1-heptene and 1-octene. For example, neither 1,3-butadiene, nor 2-butene, nor styrene are referred as α -olefins according to the present disclosure.

[0019] The term "poly- α -olefin" refers to homopolymers obtained by polymerization of α -olefins and copolymers and terpolymers obtained by oligomerization of multiple distinct α -olefins.

[0020] In this document, the term "polyolefin wax" refers to polyolefin materials, which are solid at temperatures below 40 °C and which have a semi-crystalline structure at solid state. Regarding the properties of the polyolefin waxes, a reference is made to the CD Römpp's Chemical Lexicon, Georg Thieme Verlag, Stuttgart 1995. The polyolefin waxes consist of polyolefins, which can, however, be functionalized with other monomers. Such polyolefin waxes can be obtained by thermal decomposition of branched or unbranched polyolefin plastics or by direct polymerization of olefins in the presence of metallocene or non-metallocene catalysts.

[0021] In this document, the term "paraffin wax" refers to hard, crystalline wax composed mainly of saturated paraffin hydrocarbons. The paraffin waxes are commonly obtained from petroleum distillates, derived from mineral oils of the mixed-base or paraffin-base type.

[0022] In this document, the term "silane" refers to a compounds, which have at least one, typically two or three, alkoxy groups or acyloxy groups directly bonded to the silicon atom by Si-O bonds and on the other hand, at least one organic radical bound directly to the silicon atom by an Si-C bond. For example, siloxane or silicones are not to be considered as silanes according to the present disclosure.

[0023] In this document, the term "silane group" refers to silicon-containing group bound to the organic radical of the silane via the Si-C bond. The silanes and/or their silane groups have the property of undergoing hydrolysis upon contact with moisture. The terms "silane group" and "alkoxysilane group" are used interchangeably. The term "silane-functional" denotes compounds containing silane groups. "Silane-functional polymers" are thus polymers containing at least one silane group.

[0024] In this document, the term "functionalized polymer" refers to polymers which are chemically modified so as to contain a functional group on the polymer backbone. In contrast, the term "non-functionalized polymer" designates polymers which are not chemically modified so as to contain functional groups such as epoxy, silane, sulfonate, amide, or anhydride group on the polymer backbone.

[0025] In this document, the term "softening point" refers to a temperature at which compound softens in a rubber-like state, or a temperature at which the crystalline portion within the compound melts. The softening point can be measured by a Ring and Ball method according to DIN EN 1238.

[0026] In this document, the term "molecular weight" refers to the molar mass (g/mol) of a molecule or a part of a molecule, also referred to as "moiety". The term "average molecular weight" refers to number average molecular weight (M_n) of an oligomeric or polymeric mixture of molecules or moieties. The average molecular weight can be determined by gel permeation chromatography using polystyrene as standard in a polymer solution in tetrahydrofuran.

[0027] In this document, the term "weak acid" refers to inorganic and organic acids that are only partially dissociated in aqueous solutions. Preferably, a weak acid has a pK_a value of 1.0 or more, more preferably of 2.0 or more. The term " pK_a value" refers to the negative logarithm of the ionization constant (" K_a ").

[0028] In this document, the term "strong acid" refers to inorganic and organic acids that are substantially completely dissociated in aqueous solutions. Preferably, a strong acid has a pK_a value of less than 0, more preferably less than -1.0.

[0029] The composition for use in removing a reactive adhesive from production, processing and application devices of the present invention comprises at least one thermoplastic polymer that is solid at 25°C.

[0030] The at least one thermoplastic polymer can have a softening point measured by Ring and Ball method according to DIN EN 1238 in the range from 60 to 200°C. Preferably, the at least one thermoplastic polymer has a softening point measured by Ring and Ball method according to DIN EN 1238 in the range from 70 to 180°C, more preferably in the range from 80 to 160°C.

[0031] Preferably, the at least one thermoplastic polymer has an average molecular weight (M_n) in the range of 1500 - 75,000 g/mol, more preferably 1500 - 50,000 g/mol, most preferably 3000 - 25,000 g/mol.

[0032] The total amount of the at least one thermoplastic polymer can be more than 30.0 % by weight, preferably at least 50.0 % by weight, more preferably 60.0 - 95.0 % by weight, even more preferably 70.0 - 95.0 % by weight, most preferably 85.0 - 95.0 % by weight, based on the total weight of the composition for use in removing a reactive adhesive from production, processing and application devices.

[0033] The at least one thermoplastic polymer, which is solid at 25 °C can be a homopolymer or copolymer of unsaturated monomers, selected, for example, from the group consisting of ethylene, propylene, butylene, isobutylene, isoprene, vinyl acetate and vinyl ester with C_3 to C_{12} carboxylic acids, styrene, and (meth)acrylate. In the context of the present disclosure, the term "(meth)acrylate" designates both esters of acrylic acid and methacrylic acid.

[0034] Preferred thermoplastic polymers are poly- α -olefins, in particular amorphous poly- α -olefins (APAO), polypropylene and polyethylene homopolymers, ethylene-vinyl acetate (EVA), and styrene block copolymers, in particular low-viscosity styrene block copolymers.

[0035] Preferable amorphous poly- α -olefins include amorphous atactic polypropylene, amorphous propylene-ethylene copolymer, amorphous propylene-butene copolymer, amorphous propylene-hexene copolymer, and amorphous propylene-ethylene-butene terpolymer. Suitable amorphous poly- α -olefins can be obtained by Ziegler-Natta catalyzed polymerization or by metallocene catalyzed polymerization. Preferably, the amorphous poly- α -olefin has an average molecular weight in the range of 1500 - 50,000 g/mol, more preferably 3000 - 25,000 g/mol.

[0036] Preferred styrene block copolymers include block copolymers of type S-X-S, wherein the S designates a styrene block and X an elastic α -olefin block. The elastic α -olefin block has preferably a glass transition temperature in the range from -55 to -35 °C. Suitable elastic α -olefin blocks in the styrene block copolymer include ethylene/butylene (EB) blocks, which can be obtained by hydrogenation of butadiene blocks. Suitable elastic α -olefin blocks can also include modified α -olefin blocks, for example maleic acid anhydride grafted α -olefin blocks, in particular maleic acid anhydride grafted ethylene/butylene (EB) blocks.

[0037] The proportion of styrene blocks in the styrene block copolymer is preferably not more than 50 % by weight, in proportion to the total weight of the styrene block copolymer. In particular, the proportion of styrene blocks in the styrene block copolymer can be 10 - 35 % by weight, preferably 13 - 30 % by weight. Alternatively, it may be preferable to use styrene block copolymers with low amount of styrene blocks. In this case the proportion of styrene blocks in the styrene block copolymer is preferably 10 - 20 % by weight, more preferably 12 - 15 % by weight, in proportion to the total weight of the styrene block copolymer.

[0038] The styrene block copolymer has preferably a melt flow index (MFI) measured at 230°C at 2.16 kg of at least 100 g/10 min, more preferably 150 - 300 g/10 min, most preferably 190 - 250 g/10 min.

[0039] Suitable commercially available styrene block copolymers include, for example, Kraton® G 1652, Kraton® G 1657, Kraton® G 1726, Kraton® MD 1648 and Kraton® FG 1901 from Kraton® Performance Polymers.

[0040] The at least one thermoplastic polymer can be a functionalized polymer, such as a silane-grafted poly- α -olefin or a non-functionalized thermoplastic polymer. Preferably, the at least one thermoplastic polymer is selected from the group consisting of non-functionalized amorphous poly- α -olefins, non-functionalized polypropylene and polyethylene homopolymers, ethylene-vinyl acetate, and low-viscosity non-functionalized styrene block copolymers.

[0041] The composition for use in removing a reactive adhesive from production, processing and application devices of the present invention further comprises at least one hindered amine of polyalkylpiperidine type having a pK_b value of not more than 7.0, preferably in the range from 3.0 to 7.0, more preferably from 3.0 to 6.5, most preferably from 4.0 to 6.5.

[0042] The total amount of hindered amines of polyalkylpiperidine type having a pK_b value of not more than 7.0, preferably in the range from 3.0 to 7.0, more preferably from 3.0 to 6.5, most preferably from 4.0 to 6.5, can be at least

0.5% by weight, preferably 0.5 - 10.0% by weight, more preferably 0.5 - 5.0% by weight, even more preferably 0.5 - 3.5% by weight, most preferably 0.5 - 2.5% by weight, based on the total weight of the composition for use in removing a reactive adhesive from production, processing and application devices.

[0043] Preferably, the at least one hindered amine of polyalkylpiperidine type has an average molecular weight of at least 400 g/mol, preferably in the range of 500 - 5000 g/mol, most preferably of 500 - 4000 g/mol.

[0044] Suitable hindered amines (HALS) of polyalkylpiperidine type include all compounds of this type that are able to deactivate a catalyst present in the reactive adhesive for accelerating the curing reactions, for example crosslinking reactions of polymers containing functional groups. In particular, suitable hindered amines (HALS) of polyalkylpiperidine type are able to inhibit curing of a moisture curable adhesive. Such moisture curable adhesives may contain at least one silane-functional polymer and/or at least one isocyanate-functional polymer.

[0045] Particularly suitable hindered amines of polyalkylpiperidine type are commercially available as Chimassorb® 2020 FDL and Chimassorb® 944LD, Tinuvin® 783 FDL, Tinuvin® 770, and Tinuvin® 144 from BASF.

[0046] The composition for use in removing a reactive adhesive from production, processing and application devices can further comprise at least one filler. The at least one filler is preferably inert mineral filler. The inert mineral filler is preferably selected from the group consisting of mica, talc, kaolin, wollastonite, feldspar, chlorite, bentonite, montmorillonite, calcium carbonate (precipitated or ground), dolomite, quartz, silicic acids (pyrogenic or precipitated), cristobalite, calcium oxide, aluminum hydroxide, magnesium oxide, hollow ceramic spheres, hollow glass spheres, hollow organic spheres, glass spheres, colored pigments, and mixtures thereof.

[0047] Preferably, total amount of the fillers, if present in the composition for use in removing a reactive adhesive from production, processing and application devices, is 0.5 - 20.0% by weight, more preferably 1.0 - 15.0% by weight, most preferably 1.0 - 5.0 % by weight, based on the total weight of the composition.

[0048] The composition for use in removing a reactive adhesive from production, processing and application devices may further comprise at least one polyolefin resin, preferably an atactic polypropylene resin or a polyisobutylene (PIB) resin. The polyisobutylene resin can have an amount of terminal double bonds or can be without such terminal double bonds. In case the polyisobutylene resin contains terminal double bonds, these can be in alpha position or in beta position, preferably most of the double bonds, such as 50 - 90 % of the double bonds are in the alpha position with the remainder of double bonds being in the beta position.

[0049] Preferably, the at least one polyolefin resin has a softening point, measured by a Ring and Ball method according to DIN EN 1238, of less than 0 °C, more preferably -10 °C.

[0050] Preferably, the at least one polyolefin resin has an average molecular weight in the range of 250 - 5000 g/mol, more preferably 500 - 2500 g/mol. Suitable polyolefin resins have a pour point determined according to DIN 51597 in the range from -10 to +10°C, in particular from -10 to +5 °C. Suitable commercially available polyolefin resins include, for example, Glissopal® V230, V500 or V700 from BASF, Dynapak® Poly 230 from Univar GmbH (Essen, Deutschland), DAELIM® PB 950 from Daelim Industrial Co., Ltd, and Indopol® H100 from Ineos.

[0051] The total amount of polyolefin resins, if present in the composition for use in removing a reactive adhesive from production, processing and application devices, can be 0.5 - 95.0 % by weight, preferably 5.0 - 50.0 % by weight, more preferably 5.0 - 45.0 % by weight, most preferably 5.0 - 20.0 % by weight, based on the total weight of the composition.

[0052] The composition for use in removing a reactive adhesive from production, processing and application devices can further comprise at least one non-modified or modified polyolefin wax, preferably a non-modified polyolefin wax. Especially suitable polyolefin waxes have been prepared by means of metallocene catalysts. Examples of suitable polyolefin waxes include polyethylene, polypropylene, and propylene-ethylene copolymer waxes, which have been prepared by means of metallocene catalysts. These waxes are commercially available, for example, from Clariant under the trade name of Licocene®.

[0053] The total amount of polyolefin waxes, if present in the composition for use in removing a reactive adhesive from production, processing and application devices, is preferably not more than 15.0 % by weight, more preferably not more than 10.0% by weight, based on the total weight of the composition.

[0054] In addition, the composition for use in removing a reactive adhesive from production, processing and application devices can contain various additional substances and additives, for example, those selected from the group consisting of thermal stabilizers, plasticizers, optical brighteners, pigments, dyes, and desiccants. Preferred thermal stabilizers include sterically hindered phenols, such as Irganox® 1010 from BASF. However, the total amount of such additional auxiliary substances and additives is, preferably, not more than 10.0 % by weight, more preferably not more than 5.0 % by weight, based on the total weight of the composition for use in removing a reactive adhesive from production, processing and application devices.

[0055] Preferably, the reactive adhesive, which is removed from production, processing and application devices using the composition for use in removing a reactive adhesive from production, processing and application devices of the present invention, contains at least one curing catalyst.

[0056] The curing catalyst can be, for example, a compound that can catalyze the hydrolytic cleavage of the hydrolyzable groups of organosilanes and the subsequent condensation of the Si-OH group into siloxane group or a compound

that can catalyze reactions of isocyanates with hydroxyl groups. Examples of such curing catalysts include acids, bases, organometallic compounds, and organic amino compounds.

[0057] Examples of suitable curing catalysts include, for example, titanates such as tetrabutyl titanate or titanium tetraacetylacetonate; bismuth compounds such as bismuth tris-2-ethylhexanoate; tin carboxylates such as dibutyltin dilaurate (DBTL), dibutyltin diacetate, or dibutyltin diethylhexanoate; tin oxides such as dibutyltin oxide and dioctyltin oxide; organoaluminum compounds such as aluminum trisacetylacetonate; chelate compounds such as zirconium tetraacetylacetonate; amine compounds or salts thereof with carboxylic acids, such as octylamine, cyclohexylamine, benzylamine, dibutylamine, monoethanolamine, triethanolamine, diethylenetriamine, triethylenetetramine, triethylene-diamine, guanidine, morpholine, N-methylmorpholine, and 1,8-diazabicyclo-(5,4,0)-undecene-7 (DBU); and silane adhesion promoters having amino groups.

[0058] Preferably, the reactive adhesive contains at least one acidic curing catalyst. Examples of suitable acidic curing catalysts include Lewis acids, Brønsted acids such as inorganic acids and organic acids and esters thereof.

[0059] Suitable Lewis acid catalysts include carboxylates of tin, zinc, iron, lead, copper, and titanium, for example dioctyltin dilaurate (DOTL), copper(II)acetylacetonate, isopropyl triisostearoyl titanate, and butyl tin dihydroxide chloride. Preferably, the acidic curing catalyst is a Brønsted acid or an ester thereof. Suitable Brønsted acids include inorganic acids such as sulphuric acid, hydrochloric acid, and phosphoric acid; organic acids such as sulfonic acid and derivatives thereof, such as arylalkyl sulfonic acids and alkylated naphthalene monosulfonic acids, for example toluenesulfonic acid, dodecylbenzene sulfonic acid and disdinonyl-naphthalene disulfonic acid; palmitic acid, citric acid, stearic acid, acetic acid, alkanolic acids such as dodecanoic acid, and precursors of any of the compounds mentioned. Esters of Brønsted acids, for example esters of phosphoric acid and sulphonic acid, in particular esters of sulphonic acid further comprising at least one aromatic group such as acetyl-p-dodecyl benzene sulphonates, are especially preferred as acidic curing catalysts.

[0060] Preferably, the at least one acidic curing catalyst is selected from the group consisting of a weak inorganic acid, an ester of a weak inorganic acid, a strong organic acid, an ester of strong organic acid, and mixtures thereof. In particular, the acidic catalyst may be selected from the group consisting of phosphoric acid, phosphate esters, derivatives of phosphate esters, sulphonic acid, arylalkyl sulfonic acid, alkylated naphthalene sulfonic acid, sulfonic esters, derivatives of sulfonic esters, and mixtures thereof.

[0061] Suitable acidic curing catalysts are commercially available, for example, from Clariant under the trade name of Hordaphos®, for example Hordaphos® MDST and Hordaphos® CCMS; from Borden Chemicals under the trade name of Phencat®, for example Phencat® 10 (o-phosphoric acid and p-toluenesulphonic acid), Phencat® 15 (o-phosphoric acid and xylene sulphonic acid), Phencat® 381 (partial phosphate ester and p-toluenesulphonic acid), and Phencat® 382 (partial phosphate ester); from Chemische Fabrik Budenheim under the trade name of Budit®, for example Budit® 380; and from Rhodia under the trade name of Rhodafac®.

[0062] Preferably, the at least one curing catalyst is present in the reactive adhesive in an amount of 0.05 - 2.0 % by weight, more preferably 0.05 - 1.0 % by weight, most preferably 0.05 - 0.5 % by weight, based on the total weight of the reactive adhesive.

[0063] Preferably, the reactive adhesive is a moisture curable adhesive, in particular a moisture curable hot melt adhesive. Hot-melt adhesives are solvent free adhesives, which are solid at room temperature and which are applied to the substrate to be bonded in form of a melt. After cooling a moisture curable hot-melt adhesive solidifies and forms an adhesive bond with the substrate through physically and chemically occurring bonding.

[0064] Preferably, the moisture curable adhesive contains at least one silane-functional polymer. The at least one silane-functional polymer is preferably a silane group containing polyolefin, in particular silane group containing poly- α -olefin, more preferably particular a silane group containing amorphous poly- α -olefin. The silane group-containing poly- α -olefins are known to a person skilled in the art. For example, they can be produced by grafting unsaturated silanes, such as vinyl-trimethoxysilane, onto poly- α -olefins. A detailed description of the production of silane-grafted poly- α -olefins can be found, for example, in US 5,994,474 and DE 40 00 695 A1.

[0065] For example, the silane group containing poly- α -olefin can be a silane grafted copolymer or terpolymer made up of at least one of the monomers, which are chosen from ethylene, propylene, butylene and isobutylene. Particularly suitable examples of silane grafted poly- α -olefins include silane grafted polyethylene and polypropylene, in particular silane grafted polypropylene homopolymers and silane grafted polyethylene homopolymers.

[0066] The total amount of the silane group containing poly- α -olefins can be more than 30.0 % by weight, preferably 30.0 - 90.0 % by weight, more preferably 35.0 - 70.0 % by weight, most preferably 40.0 - 60.0 % by weight, based on the total weight of the moisture curable adhesive.

[0067] Preferably, the silane group-containing poly- α -olefin is a silane-grafted poly- α -olefin, in particular silane-grafted amorphous poly- α -olefin.

[0068] The silane group-containing poly- α -olefin can be a poly- α -olefin obtained by Ziegler-Natta catalyzed polymerization, to which silane groups have been grafted. The silane group-containing poly- α -olefin can also be a poly- α -olefin obtained by metallocene catalyzed polymerization, to which silane groups have been grafted.

[0069] The grafting degree of the silane-grafted poly- α -olefin is preferably greater than 0.5 % by weight, especially greater than 1.5 % by weight, relative to the weight of the non-functionalized poly- α -olefin. If a silane-grafted poly- α -olefin produced by means of the Ziegler-Natta process is used as the silane-grafted poly- α -olefin, the grafting degree is preferably between 1.0 and 8.0 % by weight, especially between 1.5 and 5.0 % by weight.

[0070] The reactive adhesive can comprise at least one silane group containing poly- α -olefin, which is produced through the grafting of silanes to a poly- α -olefin and at least one non-functionalized poly- α -olefin, preferably an amorphous poly- α -olefin. Preferably, the at least one silane group containing poly- α -olefin is present in the moisture curable adhesive in an amount of 30.0 - 70.0 % by weight, more preferably 40.0 - 60.0 % by weight and the at least one non-functionalized poly- α -olefin is present in the moisture curable adhesive in an amount of 10.0 - 40.0 % by weight, more preferably 15.0 - 35.0 % by weight, all the proportions being based on the total weight of the moisture curable adhesive.

[0071] The production of the composition for use in removing a reactive adhesive from production, processing and application devices according to the present invention can be conducted by melt-processing a mixture comprising the constituents of the composition in a mixing apparatus, kneader or extruder. The composition for use in removing a reactive adhesive from production, processing and application devices is preferably stored in form of solid granulates, flakes or as a solid block. The conversion of the produced melt of the composition to solid form can be conducted directly from the melt or during or after the cooling of the molten mixture. The composition for use in removing a reactive adhesive from production, processing and application devices is preferably stored in package, such as a metallic drum, which offers adequate protection against environmental influence and which is especially impermeable to moisture.

[0072] At the time of use, the composition for use in removing a reactive adhesive from production, processing and application devices is removed from the storage package and placed to a heating apparatus, such as a drum melter, and heated to a temperature sufficient to liquefy the solid mass. In case the composition for use in removing a reactive adhesive from production, processing and application devices is packed in a metallic drum it can be heated in the same package using a conventional plate heater. The liquefied composition can then be transferred from the heating apparatus to the apparatus to be cleaned by using the feeding arrangement of the apparatus, such as a hose and a pumping unit.

[0073] Another subject of the present invention is a method for removing reactive adhesives from production, processing and application devices, the method comprising steps of:

i) Feeding a cleaning composition of the present invention to a device such that the reactive adhesive comes in contact with the composition,

ii) Expelling the resulting mixture of the reactive adhesive and the cleaning composition from the device.

[0074] The "cleaning composition" refers here to the composition for use in removing a reactive adhesive from production, processing and application devices of the present invention. The cleaning composition fed into the device is preferably in molten form. The method for removing the reactive adhesive is preferably conducted at a temperature corresponding to the processing temperature of the reactive adhesive, typically in the range from 60 to 180 °C, in particular from 90 to 160 °C. However, it can be advantageous to conduct the method at a higher temperature in order to decrease the viscosity of the reactive adhesive being supplanted from the device. It may be advantageous to conduct the method at a temperature in the range from 150 °C to 220 °C, for example from 160 to 210 °C. The upper limit for the operation temperature depends on the constituents of the reactive adhesive to be removed and on the constituents of the cleaning composition. In particular, the operation temperature should not exceed the decomposition temperature of the thermoplastic polymers and/or the hindered amines of polyalkylpiperidine type contained in the cleaning composition and/or in the reactive adhesive.

[0075] Before feeding of the cleaning composition into the device to be cleaned, the feeding of other components, such as the components used for production of the reactive adhesive or the feeding of the reactive adhesive, in case of application device, such as coating device, is interrupted. The feeding of the cleaning composition is continued until it is assured that no other components than those contained in the cleaning composition are present at the outlet of the device. The cleaning time, i.e. the length of the time period between start and end of the feeding of the cleaning composition, depends on many individual factors, such as on the cleaning temperature and on the dimensions and geometry of the device to be cleaned.

[0076] The end of the cleaning time can be determined visually if the cleaning composition comprises a suitably chosen colorant or pigment. It is also possible to use a fixed cleaning time, which has been determined in advance for a specific device type and specific composition of the reactive adhesive.

[0077] Since the cleaning composition is able to inhibit the curing of the reactive adhesive, it is not necessary to remove the entire amount of the reactive adhesive from the device to obtain a satisfactory result. It can be, therefore, advantageous, that the cleaning time is set such that, for example, less than 90 %, preferably less than 80 % of the reactive adhesive is removed from the device during the cleaning operation. Since a removal rate of less than 100 % can be used, the cleaning time can be shortened, which results in significant savings in operative costs. The cleaned device can be left unused for a lengthy period of time without risk of formation of hardened adhesive deposits inside the device.

[0078] After the cleaning operation, the device can be loaded with a (new) reactive adhesive composition. After the start up, a small quantity of the product is preferably removed to ensure that the produced reactive adhesive is free of the hindered amines used in the cleaning composition.

[0079] Preferably, the reactive adhesive contains at least curing catalyst, more preferably at least one acidic curing catalyst selected from the group consisting of Lewis acids, Brönsted acids, esters of Brönsted acids, and mixtures thereof.

[0080] Suitable Lewis acid catalysts include carboxylates of tin, zinc, iron, lead, copper, and titanium, for example dioctyltin dilaurate (DOTL), copper(II)acetylacetonate, isopropyl triisostearoyl titanate, and butyl tin dihydroxide chloride. Preferably, the acidic curing catalyst is a Brönsted acid or an ester thereof. Suitable Brönsted acids include inorganic acids such as sulphuric acid, hydrochloric acid, and phosphoric acid; organic acids such as sulfonic acid and derivatives thereof, such as arylalkyl sulfonic acids and alkylated naphthalene monosulfonic acids, for example toluenesulfonic acid, dodecylbenzene sulfonic acid and disdinonyl-naphthalene disulfonic acid; palmitic acid, citric acid, stearic acid, acetic acid, alkanolic acids such as dodecanoic acid, and precursors of any of the compounds mentioned. Esters of Brönsted acids, for example esters of phosphoric acid and sulphonic acid, in particular esters of sulphonic acid further comprising at least one aromatic group such as acetyl-p-dodecyl benzene sulphonates, are especially preferred as acidic curing catalysts.

[0081] Preferably, the acidic curing catalyst is selected from the group consisting of a weak inorganic acid, an ester of a weak inorganic acid, a strong organic acid, an ester of strong organic acid, and mixtures thereof. In particular, the acidic catalyst may be selected from the group consisting of phosphoric acid, phosphate esters, derivatives of phosphate esters, sulfonic acid, arylalkyl sulfonic acid, alkylated naphthalene sulfonic acid, sulfonic esters, derivatives of sulfonic esters, and mixtures thereof.

[0082] Preferably, the curing catalyst is present in the reactive adhesive in an amount of 0.05 - 2.0 % by weight, more preferably 0.05 - 1.0 % by weight, most preferably 0.05 - 0.5 % by weight, based on the total weight of the reactive adhesive.

[0083] Preferably, the reactive adhesive is a moisture curable adhesive, in particular a moisture curable hot melt adhesive.

[0084] Preferably, the moisture curable adhesive contains at least one silane-functional polymer. The at least one silane-functional polymer is preferably a silane group containing polyolefin, more preferably a silane group containing poly- α -olefin.

[0085] The silane-group containing poly- α -olefin can have a softening point measured by a Ring and Ball method according to DIN EN 1238 in the range from 60 to 180 °C. Preferably, the thermoplastic silane-group containing poly- α -olefin has a softening point measured by a Ring and Ball method according to DIN EN 1238 in the range from 70 to 160 °C, more preferably in the range from 80 to 150 °C.

[0086] Preferably, the silane-group containing poly- α -olefin has an average molecular weight (M_n) in the range from 7000 to 25,000 g/mol.

[0087] The total amount of the silane-group containing poly- α -olefins can be more than 30.0 % by weight, preferably 30.0 - 90.0 % by weight, more preferably 35.0 - 70.0 % by weight, most preferably 40.0 - 60.0 % by weight, based on the total weight of the moisture curable adhesive composition.

[0088] The moisture curable hot-melt adhesive composition can comprise at least two different silane group containing poly- α -olefins. Preferably, the moisture curable hot-melt adhesive composition comprises at least one low silane-grafted poly- α -olefin, in particular at least one silane-grafted poly- α -olefin having a degree of grafting in the range of 1.0 - 3.0, and at least one high silane-grafted poly- α -olefin, in particular at least one silane-grafted poly- α -olefin having a degree of grafting in the range of 3.5 - 8.0.

[0089] The moisture curable hot-melt adhesive composition can comprise at least one poly- α -olefin, which is produced through the grafting of silanes on a poly- α -olefin, which has been produced according to the Ziegler-Natta process, as well as at least one silane grafted poly- α -olefin, which is produced through grafting of silanes on a poly- α -olefin that has been produced by means of metallocene catalysts.

[0090] The reactive adhesive can also comprise at least one silane group containing poly- α -olefin, which is produced through the grafting of silanes on a poly- α -olefin and at least one non-functionalized poly- α -olefin, preferably a non-functionalized amorphous poly- α -olefin (APAO). Preferable amorphous poly- α -olefins include amorphous atactic polypropylene, amorphous propylene-ethylene copolymer, amorphous propylene-butene copolymer, amorphous propylene-hexene copolymer, and amorphous propylene-ethylene-butene terpolymer. Suitable amorphous poly- α -olefins can be obtained by Ziegler-Natta catalyzed polymerization or by metallocene catalyzed polymerization. Preferably, the at least one non-functionalized amorphous poly- α -olefin has an average molecular weight in the range of 1500 - 50,000 g/mol, more preferably 3000 - 25,000 g/mol.

[0091] Preferably, the at least one silane group containing poly- α -olefin is present in the moisture curable adhesive in an amount of 30.0 - 70.0 % by weight, more preferably 40.0 - 60.0 % by weight and the non-functionalized poly- α -olefin is present in the moisture curable adhesive in an amount of 10.0 - 40.0 % by weight, more preferably 15.0 - 35.0 % by weight, all the proportions being based on the total weight of the moisture curable adhesive.

[0092] The moisture curable adhesive can further comprise at least one resin that is tackifying at 25 °C. Suitable

tackifying resins include medium- to high-molecular weight compounds selected from the group consisting of hydrocarbon resins, polyolefins, polyesters, polyethers, poly(meth)acrylates and amino resins.

[0093] The at least one tackifying resin has preferably a softening point measured by a Ring and Ball method according to DIN EN 1238 in the range from 50 to 150°C, more preferably from 70 to 130°C, most preferably from 80 to 120°C.

[0094] Suitable commercially available hydrocarbon resins include, for example, Wingtack® 10 and Wingtack® 86 from Cray Valley, Escorez® 5040 from Exxon Mobile Chemical, Picco® A10, Regalite® R1010 from Eastman Kodak, and Hikorez® A-2115 from Kolon Industries.

[0095] Other suitable tackifying resins include, for example, polyterpene resins, such as Silvares® TR A25 from Arizona Chemical, rosin esters and/or tall oil rosin esters, such as Silvatac® RE12, Silvatac® RE10, Silvatac® R15, Silvatac® RE20, Silvatac® RE25 and Silvatac® RE40 from Arizona Chemical.

[0096] The moisture curable hot-melt adhesive can further comprise at least one non-modified or modified polyolefin wax. Suitable modified polyolefin waxes include polar-modified, such as α - and β -unsaturated carboxylic acid, (meth)acrylic acid and maleic anhydride modified polyolefin waxes and silane-modified polyolefin waxes. Suitable maleic anhydride functionalized polyolefin waxes include waxes of ethylene and propylene homo- and copolymers grafted with maleic anhydride, in particular, a polypropylene or polyethylene wax grafted with maleic anhydride. Suitable silane modified polyolefin waxes include waxes of ethene and propene homo- and copolymers grafted with silane, in particular, a polypropylene or polyethylene wax grafted with silane.

[0097] According to another aspect of the present invention, use of the cleaning composition according to the present invention for removing reactive adhesives, preferably moisture curable polyolefin hot-melt adhesives, from production, processing and application devices, is provided. The cleaning composition refers here to the composition for use in removing a reactive adhesive from production, processing and application devices of the present invention.

Examples

[0098] The followings compounds and products shown in Table 1 were used in the examples.

Table 1

Hordaphos® MDST	Phosphoric acid ester catalyst	Clariant
Chimassorb® 2020 FDL	Oligomeric N-H HALS	BASF
Chimassorb® 944 LD	Oligomeric N-H HALS	BASF
Tinuvin® 783 FDL	Blend of oligomeric N-H and N-alkyl HALS	BASF
Tinuvin® 770	N-H HALS, $pk_b = 4 - 5$	BASF
Tinuvin® 144	N-alkyl HALS, $pk_b = 5 - 6$	BASF
Tinuvin® 622	Oligomeric N-alkyl HALS, $pk_b = 7 - 8$	BASF
Tinuvin® 326	BTZ ultraviolet light absorber	Ciba
Tinuvin® 152	N-OR HALS, $pk_b = 8 - 10$	BASF
Irganox® 1010	Phenolic antioxidant	Ciba
Ceridust® 3910	Micronized amide wax	Hoechst
Lignostab® 1198	N-OH HALS	Ciba

Test compositions

[0099] The compositions from Ex 1 to Ex 5 contain a hindered amine light stabilizer (HALS), which is able to inhibit or at least significantly slow down the curing reaction of the moisture curable adhesive. The compositions from Ref Ex6 to Ref Ex12 are comparative compositions containing a HALS or an UV-stabilizer, which are not able to inhibit the curing reaction of the adhesive.

[0100] The moisture-curable hot-melt adhesive used in the examples contained:

- 20.0 - 25.0 % by weight of a commercially available amorphous poly- α -olefin,
- 55.0 - 65.0 % by weight of a commercially available silane-grafted amorphous poly- α -olefin,
- 5.0 - 10.0 % by weight of a commercially available maleic anhydride grafted polypropylene wax,
- 5.0 - 10.0 % by weight of a commercially available hydrocarbon resin, and

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0.15 % by weight of a Hordaphos® MDST catalyst available from Clariant.

[0101] The test compositions as presented in Table 2 were prepared according to the procedures as presented below.

Preparation of test compositions Ex 1 to Ref Ex 12

[0102] The moisture curable hot-melt adhesive was provided in a tin can of a standard laboratory reactor and mixed at a temperature of 160 °C with a stirrer speed of 100 rpm and at vacuum of 100 mbar for a time period of 15 min. After completion of stirring, the rest of the components were added to the mixture. After the addition, the mixing was continued for 15 minutes at a temperature of 160 °C and at vacuum of 100 mbar.

Curing behavior

[0103] A sample composition provided in a sealed tube was preheated in an oven to at temperature of 160 °C for a time period of 30 minutes. After the heating, a sample of 20 g of the molten adhesive was applied with a doctor blade to surface of a silicone paper (B700 white, Laufenberg & Sohn KG) strip placed on a heating plate having a temperature of 160 °C. The silicone paper had dimensions of 30 cm x 6 cm and the adhesive was applied as a film having a thickness of 500 µm and dimensions of 30 cm x 6 cm. Before applying the adhesive film, the silicone paper strip and the doctor blade were heated to a temperature of 160 °C with the heating plate.

[0104] Immediately after application of the adhesive, the silicone paper strip was removed from the heating plate and stored at standard climatic conditions (20°C, 55 % relative humidity). The point of time when the adhesive film was solidified was recorded as the starting point of the curing measurement. At defined sampling times, a test strip having dimensions of 10 cm x 1 cm was cut from the silicone coated paper having film of adhesive on its surface and placed on a heating plate having a temperature of 150 °C. The procedure was continued until the adhesive film of the test strip no longer melted on the heating plate. The curing results after 24 hours, 48 hours, one week, and after more than four weeks are presented in Tables 2 and 3.

Table 2

Composition [wt.-%]	Ex1	Ex2	Ex3	Ex4	Ex5	Ref Ex6
Reactive HM-adhesive	98.5	98.5	98.5	98.5	98.5	100
Chimassorb 2020 FDL	1.5					
Chimassorb 944 LD		1.5				
Tinuvin 783 FDL			1.5			
Tinuvin 770				1.5		
Tinuvin 144					1.5	
Tinuvin 622						
Tinuvin 326						
Tinuvin 152						
Irganox 1010						
Ceridust 3910						
Lignostab 1198						
Curing result 24 h	Not cured	Not cured	Not cured	Not cured	Not cured	Cured
Curing result 48 h	Not cured	Not cured	Not cured	Not fully cured	Cured	Cured
Curing result 1 week	Not cured	Not cured	Not cured	Cured	Cured	Cured
Curing result > 4 weeks	Not cured	Cured	Cured	Cured	Cured	Cured

Table 3

Composition [wt.-%]	Ref Ex7	Ref Ex8	Ref Ex9	Ref Ex10	Ref Ex11	Ref Ex12
Reactive HM-adhesive	98.5	98.5	98.5	98.5	95.24	98.5
Chimassorb 2020 FDL						
Chimassorb 944 LD						
Tinuvin 783 FDL						
Tinuvin 770						
Tinuvin 144						
Tinuvin 622	1.5					
Tinuvin 326		1.5				
Tinuvin 152			1.5			
Irganox 1010				1.5		
Ceridust 3910					4.76	
Lignostab 1198						1.5
Curing result 24 h	Cured	Cured	Cured	Cured	Cured	Cured
Curing result 48 h	Cured	Cured	Cured	Cured	Cured	Cured
Curing result 1 week	Cured	Cured	Cured	Cured	Cured	Cured
Curing result > 4 weeks	Cured	Cured	Cured	Cured	Cured	Cured

Claims

1. A composition for use in removing a reactive adhesive from production, processing and application devices, the composition comprising:
 - a) at least one thermoplastic polymer that is solid at 25 °C, and
 - b) at least one hindered amine of polyalkylpiperidine type having a pK_b value of not more than 7.0, preferably in the range from 4.0 to 6.5.
2. The composition for use in removing a reactive adhesive from production, processing and application devices according to claim 1, wherein
 - a) the at least one thermoplastic polymer is present in an amount of at least 50.0 % by weight, preferably 70.0 - 95.0 % by weight, most preferably 85.0 - 95.0 % by weight, and
 - b) the at least one hindered amine of polyalkylpiperidine type is present in an amount of at least 0.5 % by weight, preferably 0.5 - 5.0 % by weight, most preferably 1.0 - 2.5 % by weight, all the proportions being based on the total weight of the composition.
3. The composition for use in removing a reactive adhesive from production, processing and application devices according to claim 1 or 2, wherein the hindered amine of polyalkylpiperidine type has an average molecular weight of at least 400 g/mol, preferably in the range of 500 - 5000 g/mol, most preferably from 500 - 4000 g/mol.
4. The composition for use in removing a reactive adhesive from production, processing and application devices according to any of previous claims, wherein the reactive adhesive contains at least one acidic curing catalyst.
5. The composition for use in removing a reactive adhesive from production, processing and application devices according to claim 4, wherein the acidic curing catalyst is selected from the group consisting of a weak inorganic acid, an ester of a weak inorganic acid, a strong organic acid, an ester of a strong organic acid, and mixtures thereof.
6. The composition for use in removing a reactive adhesive from production, processing and application devices

according to any of previous claims, wherein the reactive adhesive is a moisture curable adhesive.

7. The composition for use in removing a reactive adhesive from production, processing and application devices according to any of previous claims, wherein the reactive adhesive contains at least one silane-functional polymer, preferably at least one silane-functional poly- α -olefin.
8. The composition for use in removing a reactive adhesive from production, processing and application devices according to any of previous claims, wherein the at least one thermoplastic polymer is selected from the group consisting of amorphous poly- α -olefins, polypropylene homopolymers, polyethylene homopolymers, ethylene - vinyl acetate copolymers (EVA), and styrene block copolymers.
9. A method of removing reactive adhesives from production, processing and application devices, the method comprising steps of:
 - i) Feeding a composition as defined in any of claims 1-8 to a device such that the reactive adhesive comes in contact with the composition,
 - ii) Expelling the resulting mixture of the reactive adhesive and the composition from the device.
10. The method according to claim 9, wherein the reactive adhesive contains at least one acidic curing catalyst.
11. The method according to claims 10, wherein the at least one acidic curing catalyst is selected from the group consisting of a weak inorganic acid, an ester of a weak inorganic acid, a strong organic acid, an ester of a strong organic acid, and mixtures thereof.
12. The method according to any of claims 9-11, wherein the reactive adhesive is a moisture curable adhesive.
13. The method according to any of claims 9-12, wherein the reactive adhesive contains at least one silane-functional polymer, preferably at least one a silane-functional poly- α -olefin.
14. The method according to claim 13, wherein the at least one silane-functional polymer is present in the reactive adhesive in an amount of at least 30.0 % by weight, preferably 35.0 - 70.0 % by weight, based on the total weight of the reactive adhesive.
15. Use of the composition as defined in any of claims 1-8 for removing a reactive adhesive from production, processing and application devices.



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Application Number
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