The present invention relates to two-part polyurethane compositions. This two-part composition consists of a first pack (C1) and a second pack (C2). The first pack (C1) comprises at least one hyperbranched copolymer (HBC) having pending OH groups and which is prepared from at least one or more monomer(s) (M2) having at least two unsaturated C-C bonds and one or more monomer(s) (M3) having one unsaturated C-C bonds and one hydroxyl group in the presence of a cobalt (II) complex (CC). The second pack (C2) comprises at least one polyisocyanate (PI). It has been possible to offer a two-part polyurethane composition which has low viscosity, long pot life, fast cure, excellent weathering and UV resistance and is particularly suitable for the use as coating.
TWO-PART POLYURETHANES BASED ON HYPERBRANCHED POLYMERS

Technical field

The invention relates to the field of two-part polyurethane compositions.

Background of the invention

Two-part polyurethane is a well-established technology for a variety of applications. Particularly known are two-part polyurethane compositions in which one part comprises polyol(s) and the second part comprises polyisocyanate(s). As polyols a wide range of molecules is known, such as polyether polyols, polyester polyols and acrylic polyols. These known two-part polyurethanes are particularly fast curing. Furthermore, they have also a short pot-life, which is problematic for certain applications, particularly for application of larger area of application. Furthermore, they also tend, unfortunately, to have a rather high viscosity after mixing. In order to reduce the viscosity additional solvents is used. However, this contravenes the trend of more stringent regulations in the market to ask for of a reduction of solvents or VOC (Volatile Organic Compounds) which is based on ecological and ecotoxic reasons.

Hyperbranched polymers are a recently found class of polymers and could be obtained from different monomers having unsaturated C-C bonds. Hyperbranched polymers have a particular different structure than traditional polymers, particularly Polyols, which are either linear or only slightly branched. Hyperbranched polymers exhibit a branched structure. It is very advantageous that hyperbranched polymers can be made through one-pot synthesis and therefore are very cost effective.

US 4,880,889 discloses a preparation of hydroxyl functional acrylic polymer with monomers having more than one C-C double bonds using a mercapto compound as chain stopper, being effectively a chain transfer agents for the radical polymerization process.
US 576721 discloses the preparation of (meth)acrylate functional hyperbranched polymers used for photopolymerization using a cobalt (II) complex as chain transfer catalyst. WO 98/04603 A1 discloses a thermoformable cast being directly formed by the polymerization of different (meth)acrylic monomers in the presence of cobalt (II) complexes, particularly of a bis(borondifluorodimethylglyoximate) cobaltate (II) complex.


US 5,115,064 discloses isocyanate functional acrylic copolymers being prepared from the free radical polymerization of isocyanatoalkyi esters of (meth)acrylic acid in the presence of mercapto compounds as regulators, which then in a second step may be crosslinked by polyols.

Summary of the invention

The problem to be solved by the present invention is to offer a two-part polyurethane composition which has an extended pot-life on the one side but having a fast curing behaviour on the other side and which shows excellent UV stability.

It has been found that a two-part composition according to claim 1 is able to solve this problem in an unexpected manner.

Particularly, it has been found that the present two-part composition after mixing has a relatively low viscosity, which leads relates to the advantages of either using less solvent or to increase the amount of fillers and, hence, still offer an acceptable workability.

Surprisingly, it has been found that the two-part composition has -in comparison to corresponding two-part compositions according to the technology of the state of the art- an extend pot-life easily allowing also large area applications combined with a very fast cure. This is a rather exceptional behaviour as fast curing normally correlates also to short pot-life. In other
words the two-part polyurethane composition can be applied for a longer time on a surface, however, after the pot-life the development of strength is very rapid and high green strengths are obtained after very short time, particularly under heated conditions. This combination is particularly advantageous for application of the two-part polyurethane composition as a coating or an adhesive, particularly in application where the composition is applied on larger objects. It is also beneficial to users who apply and cure the coating in a production line such as automotive OEM coating application where the production time can be shortened and the heating energy can be reduced.

Very surprisingly, it has been also found that the two-part polyurethane composition has an excellent UV stability which is not the case if a hyperbranched polyols being prepared by radical polymerization of the corresponding monomers using mercapto compounds as chain transfer agent would be used in the formulation instead.

Therefore, it has been possible to offer a two-part polyurethane composition which has low viscosity, long pot life, fast cure, excellent weathering and UV resistance, flexibility and adhesion and is particularly suitable for the use as coating.

Furthermore, it has been found that a reaction product having pending NCO groups according to claim 16 can be easily prepared from the two-part polyurethane composition of invention and which has particular advantageous properties and is very interesting for the preparation of polyurethanes with very high mechanical properties.

Further aspects of the invention are subject matter of further independenting claims. Particularly preferred embodiments of the invention are the subject matter of the subclaims.

**Detailed description of the invention**

The present invention relates to two-part polyurethane composition. This two-part composition consists of a first pack (C1) and of a second pack (C2). The first pack (C1) comprises at least one hyperbranched copolymer (HBC) having pending OH groups and which is prepared from at least
a) one or more monomer(s) (M2) having at least two unsaturated C-C bonds
b) one or more monomer(s) (MH) having one unsaturated C-C bonds and one hydroxyl group

in the presence of a cobalt (II) complex (CC). The second pack (C2) comprises at least one polyisocyanate (PI).

The term "polyisocyanate" in the present document encompasses compounds having two or more isocyanate groups, independently of whether they are monomeric diisocyanates, oligomeric polyisocyanates, or polymers containing isocyanate groups and having a relatively high molecular weight (typically larger than 1000 g/mol).

The term "polymer" in the present document encompasses on the one hand a collective of macromolecules which, while being chemically uniform, nevertheless differ in respect of degree of polymerization, molar mass, and chain length, and have been prepared by a polymerization reaction (chain-growth addition polymerization, polyaddition, polycondensation, radical polymerization). The term also, moreover, encompasses derivatives of such a collective of macromolecules from polymerization reactions, in other words compounds which have been obtained by means of reactions, such as additions or substitutions, for example, of functional groups on existing macromolecules, and which may be chemically uniform or chemically non-uniform. The term also encompasses, furthermore, what are known as prepolymer, by which are meant reactive oligomeric pre-adducts whose functional groups take part in the construction of macromolecules.

In the present document, substance names beginning with "poly", such as polyisocyanate or polyol, denote substances which, in a formal sense, contain two or more of the functional groups which occur in their name per molecule.

"Room temperature" means in the present document a temperature of 23°C.

The person skilled in the art in this field uses frequently the term "two component" instead of the term "two-part" mentioned before. In any of these cases a chemically reactive system is meant which comprises of individual
reactive ingredients which are stored in two separate compartments, respectively packs, in order to avoid the spontaneous reaction between said reactive ingredients.

In the present document, the bold-labelling of references such as C1, C2,HBC,CC,PI,M1 ,Mr,M2,M2',MH,MH',IN, PI-O, PI-M, PUP, HBC-NCO, S or the like are used only for better reading comprehension and identification.

The first pack (C1) (first component) comprises at least one hyperbranched copolymer (HBC) having pending OH groups. Said hyperbranched copolymer (HBC) having pending OH groups is prepared from at least one or more monomer(s) (M2) having at least two unsaturated C-C bonds and one or more monomer(s) (MH) having one unsaturated C-C bonds and one hydroxyl group in the presence of a cobalt (II) complex (CC).

It is important to realize that the presence at least two different types of monomers for the production of the hyperbranched copolymer (HPC) is necessary. It is preferred that at least one (meth)acrylic ester and at least one hydroxyl-functional (meth)acrylic ester are present.

Monomer(s) (M2) having at least two unsaturated C-C bonds are in one embodiment particularly di(meth)acylates which are (poly)alkylene or (poly)oxyalkylene bridged di(meth)acylates.

Preferably said di(meth)acrylate is of formula (I-a) or (I-b):

$$\text{(I-a)}$$

$$\begin{align*} &\text{O} \\
&\text{O} \text{-} \text{R}^2 \text{-} \text{O} \\
&\text{O} \text{-} \text{R}^1 \text{-} \text{O} \\
&\text{O} \\
\end{align*}$$

$$\text{(I-b)}$$

$$\begin{align*} &\text{O} \\
&\text{O} \text{-} \text{R}^3 \text{-} \text{O} \\
&\text{O} \text{-} \text{R}^1 \text{-} \text{O} \\
&\text{O} \\
\end{align*}$$

wherein \( R^1 \) is H or a methyl group, preferably a methyl group;
\( R^2 \) is a linear or branched alkylene group with 2 to 30 carbon atoms, particularly 2 to 15 carbon atoms, preferably an ethylene, propylene, isopropylene or butylene group; \( R^3 \) is a linear or branched alkylene group with 2 to 6 carbon atoms and \( n \) is an integer from 2 to 6.

In a further embodiment the alkylene group \( R^2 \) has some aromatic moieties in the backbone and the di(meth)acrylate is, hence, particularly of the formula \((l-a')\)

\[
\begin{align*}
R^1 & \quad \text{O} \quad [R^5 \quad \text{O}]_{n'} \quad [\text{O} \quad R^6] \quad R^1
\end{align*}
\]

\((l-a')\)

wherein \( R' \) and \( R'' \) are \( H \) or \( CH_3 \), \( R^5 \) and \( R^6 \) are independently from each other \( H \), \( CH_3 \) or \( CH_2CH_3 \), \( n' \) is a value of 1 up to 6 and \( R^1 \) is as defined for formula \((l-a)\), respectively \((l-b)\).

In a further embodiment such monomers \((M2)\) having at least two unsaturated C-C bonds are bis(meth)acrylamides of diamines of the formula

\[
NH_2-R^2-NH_2 \quad \text{or} \quad NH_2-[R^3-0]_n-R^3-NH_2
\]

wherein \( R^2 \), \( R^3 \) and \( n \) are as defined for formula \((l-a)\), respectively \((l-b)\).

In a further embodiment such monomers \((M2)\) having at least two unsaturated C-C bonds are monomers having three or more, particularly three or four, unsaturated C-C bonds. Examples of such monomers esters of (meth)acrylic acids and triol or tetrol, such as trimethylolpropane tri(meth)acrylate, trimethylolethane tri(meth)acrylate, glycerol tri(meth)acrylate or pentaerythritol tri(meth)acrylate or pentaerythritol tetra(meth)acrylate.

However, monomer(s) \((M2)\) having at least two unsaturated C-C bonds are preferably monomer(s) having exactly two unsaturated C-C bonds.
Particularly useful as monomer(s) (MH) having one unsaturated C-C bonds and one hydroxyl group are hydroxyalkyl(meth)acrylates. Preferably such hydroxyalkyl(meth)acrylates are the ones of formula (II)

\[ \text{II} \]

wherein \( R^1 \) is H or a methyl group, preferably a methyl group, and \( R^4 \) is a linear or branched alkenylene group of 1 to 10 carbon atoms, particularly a methylene or ethylene or propylene or butylene group.

Preferred such monomers (MH) are such as hydroxyethylacrylate (HEA), hydroxyethylmethacrylate, (HEMA), hydroxypropylacrylate (HPA), hydroxypropylmethacrylate (HPMA), hydroxybutylacrylate (HBA) or hydroxybutylmethacrylate (HBMA).

In certain cases also monomer(s) having one unsaturated C-C bonds and two or more one hydroxyl group can be used as additional monomers. Examples for such monomers are monooesters of (meth)acrylic acid and a polyol, such as (meth)acrylic monoester of glycerol or trimethylolpropane or trimethylolethane or pentaerythritol.

In certain cases also monomer(s) having two or more unsaturated C-C bonds and at least one hydroxyl group can be used as additional monomers. Examples for such monomers are diesters of (meth)acrylic acid and a triol or a tetrol such as trimethylolpropane di(meth)acrylate, trimethylolethane di(meth)-acrylate, glycerol di(meth)acrylate or pentaerythritol di(meth)acrylate or triesters of (meth)acrylic acid and a tetrol such as pentaerythritol tri(meth)acrylate.

Further examples of such monomer(s) are obtained from the reaction of (meth)acrylic acid and a polyepoxide, such as the following formula:
wherein $R^1$, $R'$ and $R''$ are as defined for formula (l-a').

In addition to the monomer(s) (M2) having at least two unsaturated C-C bonds and to monomer(s) (MH) having one unsaturated C-C bond and one hydroxyl group, in further embodiments additional monomer(s) (M1) having exactly one unsaturated C-C bonds may be used for the preparation for the hyperbranched copolymer (HBC).

Such monomers (M1) are preferably alkyl(meth)acrylates (M1'). Preferred alkyl(meth)acrylates are esters of (meth)acrylic acids and alkyl alcohols having 1 to 16, particularly 1 to 9 carbon atoms. More preferably the alkyl(meth)acrylate (M1') is selected from the group consisting of methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, cyclohexyl-(meth)acrylate, hexyl(meth)acrylate, ethylhexyl(meth)acrylate isobornyl(meth)-acrylate, trimethylcyclohexyl(meth)acrylate, 2-ethylhexyl(meth)acrylate.

Furthermore also esters of (meth)acrylic acid of monoalcohols having hetero atoms, particularly in form of ether groups, are suitable as monomer(s) having unsaturated C-C bonds are monomers (M1), such as tetrahydrofurfuryl(meth)acrylate.

Furthermore, also styrene, butadiene or isoprene may be used in certain cases as monomers having one unsaturated C-C bonds.

Particularly suitable monomers having unsaturated C-C bonds are acrylic acid, esters of acrylic acid, amides of acrylic acid, methacrylic acid, esters of methacrylic acid, amides of methacrylic acid.

The preparation of the hyperbranched copolymer (HBC) having pending OH groups is made in the presence of a cobalt (II) complex (CC). Such cobalt (II) complexes serve as Chain Transfer Catalyst (CTC).

Particularly suitable as cobalt (II) complexes are cobalt (II) porphyrin complexes or those cobalt(II) chelates disclosed in US 4,694,054, which is incorporated herein by reference in their entirety.

The cobalt (II) complex (CC) is particularly a cobaloxime.
Particularly preferred as cobalt (II) complex (CC) are cobalt(II) complexes of formula (III) and (III'). Particularly cobalt (II) complex (CC) is a bis(borondifluorodimethylglyoximate) cobaltate (II) complex. This Co (II) complex may be represented by the following formula (III').

In formula (III), Y, independently, is phenyl or a alkyl group with 1 to 12 carbon atoms or Y and Y on adjacent carbon atoms, taken together, is a alkylene group with 4 to 6 carbon atoms or is a -CH=CH=CH=CH-.

It is clear to the person skilled in the art that there might be additionally be some further ligands such as solvents or water attached to the central Co(II) atom, and, hence, particularly leading to an octahedral structure, respectively pseudo-octahedral structure.

The synthesis of the bis(borondifluorodimethylglyoximate) cobaltate (II) complex (often also abbreviated as CoBF respectively COBF) is described in detail in A.Bakac et al., *J. Am. Chem. Soc.* **1984**, *106*, 5197-5202, which is incorporated herein by reference in its entirety.

The cobalt (II) complex (CC), particularly the bis(borondifluorodimethylglyoximate) cobaltate (II) complex, is preferably used in the preparation of the hyperbranched copolymer (HBC) in a concentration of less than 1 % by weight, particularly less than 0.5 % by weight, preferably of 0.001 to 0.1 % by weight, relative to the weight of the monomers having unsaturated C-C bonds.
Details for the preparation of hyperbranched polymers (HBC) can be found in US 4,880,889 and US 5,767,211 which disclosure is hereby incorporated by reference in their entirety.

Preferably, the production of the hyperbranched polymers (HBC) is made in the presence of a non-peroxide initiator (IN). Particularly useful are azo initiators such as 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2-azobis-(4-methoxy-2,4-dimethylvaleronitrile), 2,2-azobis-(2,4-dimethylvaleronitrile), (1-phenylethyl)azodiphenylmethane, 2,2-azobis-(isobutyronitrile), dimethyl 2,2-azobis-(isobutyrate), 2,2-azobis-(2-methylbutyronitrile), 1,1-azobis-(1-cyclohexanecarbonitrile), 2,2-azobis-(2,4,4-trimethyl pentane), 2,2-azobis-2-methylpropane), 2,2-azobis(N,N-dimethylene isobutyronidine)dihydrochloride, 2,2-azobis-(2-amidno propane)dihydrochloride, 2,2-azobis-(N,N-dimethyleneiso- butyronidine), 4,4-azobis-(4-cyanopentanoic acid) and 3,3-azobis-(3cyano-butyrsulfonic acid). Most preferred as non-peroxide initiator (IN) is 2,2-azobis-(isobutyronitrile) (AIBN).

In a preferred embodiment the hyperbranched copolymer (HBC) is prepared from

a') one or more monomer(s) having at least two unsaturated C-C bonds (M2);

b') one or more monomer(s) having one unsaturated C-C bonds (MH) and one hydroxyl group;

c') one or more monomer(s) having one unsaturated C-C bonds (M1) in the presence of a non-peroxide initiator (IN) and the cobalt (II) complex (CC).

In a more preferred embodiment the hyperbranched copolymer (HBC) is prepared from

a'') one or more di(meth)acrylate(s) (M2');

b'') one or more hydroxyalkyl(meth)acrylate(s) (MH') and

c'') one or more alkyl(meth)acrylate(s) (M1') in the presence of an azo initiator, particularly 2,2-azobis-(isobutyronitrile), and the cobalt (II) complex (CC).

More preferably, the hyperbranched copolymer (HBC) is prepared from
1 - 20 % by weight, particularly 1.5 - 15 % by weight, of di(meth)acrylate (M2'),
related to the weight sum of di(meth)acrylate (M2') and Hydroxyalkyl-
(meth)acrylate(s) (MH') and alkyl(meth)acrylate(s) (M1');
10 - 45 % by weight, particularly 15 - 35 % by weight, of hydroxyalkyl(meth)-
acrylate(s) (MH'), related to the weight sum of di(meth)acrylate (M2') and
hydroxyalkyl(meth)acrylate(s) (MH') and alkyl(meth)acrylate(s) (M1')
and
30-80% by weight, particularly 60-75% by weight, of alkyl(meth)acrylate(s) (M1'),
related to the weight sum of di(meth)acrylate (M2') and hydroxy-
alkyl(meth)acrylate(s) (MH') and alkyl(meth)acrylate(s) (M1');
in the presence of an azo initiator, particularly 2,2-azobis-(isobutynitrile), and
the cobalt (II) complex (CC).

The polymerization reaction of the above composition(s) is typically
carried out at high temperatures (60 - 400°C) by way of the addition of mixture
of monomer(s)/CTC/initiator into a heated solvent at above mentioned high
temperatures. The product obtained is generally a hyperbranched polymer in
solution with relatively low viscosity and in high conversion of monomers (90-
99%) with no gel. The resulted product, i.e. the hyperbranched polyol in the
solvent has a typical viscosity ranging from 3000 to 18000 mPa*s (cP) at
20°C. The hyperbranched copolymer (HBC) having pending OH groups may
be purified, however, it may also be used as such. In said resulted product,
respectively in the hyperbranched copolymer (HBC) having pending OH
groups, there may remain some residuals of the cobalt (II) complex (CC).

Typically, polymerizations is conducted in 80 % by weight butyl acetate
solution, to which a mixture of 3.2 % by weight of ethylene glycol dimethacry-
late (EGDMA), 31 % by weight of methylmethacrylate (MMA), 28 % by weight
of hydroxypropylmethacrylate (HPMA), 16 % by weight of butylmethacrylate
(BMA), 1.2 % by weight of 2,2'-azobis(isobutynitrile)(AIBN) and 45 ppm
cobalt (II) complex (CC) is added over a period of time during which the tem-
perature is maintained within 80-1 40°C. After the addition the mixture is stirred
for a further period of time at above 60°C until the reaction is finished. Sample
is taken for 1H NMR analysis to assess the conversion of the unsaturated monomers. The resulted product is cooled, filtered and ready to be used as a polyol component. The resulted product contains hyperbranched polyol in butyl acetate has a viscosity ranging from 3000 to 18000 mPa*s (cP) at 20°C.

The first pack (C1) may also comprise further ingredients which are principally known to the person skilled in the art in the field of two component polyurethanes. Particularly useful additional ingredients of the first pack are plasticizers, solvents, inorganic and organic fillers, catalysts, particularly for catalyzing the NCO/OH reaction, rheology modifiers, driers, adhesion promoters, stabilizers against heat, light and UV radiation, flame retardants, biocides, pigments or surface-active substances as for example wetting agents, flow control agents, de-aerating agents or defoamers.

It is advantageous to ensure that such additional ingredients do not adversely affect the stability of the first pack (C1) in storage. This means that these ingredients not give rise to any significant extent, in the course of storage, to the reactions that lead to reactions, particularly to crosslinking. Therefore, these optional ingredients should particularly not react with the other ingredients in said pack, particularly not with hyperbranched copolymer (HBC) having pending OH groups, or trigger some reaction of ingredients being present in the first pack.

The second pack (C2) (second component) comprises at least one polyisocyanate (PI).

In one embodiment the polyisocyanate (PI) is a monomeric polyisocyanate (PI-M), particularly a monomeric diisocyanate or triisocyanate. Said monomeric polyisocyanate may be an aromatic or an aliphatic polyisocyanate.

"Aromatic polyisocyanate" identifies an organic compound which contains exclusively aromatic isocyanate groups. "Aromatic" identifies an isocyanate group which is attached to an aromatic or heteroaromatic radical. "Aliphatic polyisocyanate" identifies an organic compound which contains
aliphatic isocyanate groups. "Aliphatic" identifies an isocyanate group which is attached to an aliphatic, cycloaliphatic or arylaliphatic radical.

Examples of suitable aromatic monomeric polyisocyanates include polyisocyanates such as 2,4- and 2,6-tolylene diisocyanate and any desired mixtures of these isomers (TDI), 4,4'-, 2,4'- and 2,2'-diphenylmethane diisocyanate and any desired mixtures of these isomers (MDI), 1,3- and 1,4-phenylene diisocyanate, 2,3,5,6-tetramethyl-1,4-diisocyanatobenzene, naphthalene-1,5-diisocyanate (NDI), 3,3'-dimethyl-4,4'-diisocyanatobiphenyl (TODI), dianisidine diisocyanate (DADI), 1,3,5-tris(isocyanatomethyl)benzene, tris(4-isocyanatophenyl)methylene and tris-(4-isocyanatophenyl) thiophosphate.

Examples of suitable aliphatic monomeric polyisocyanates include polyisocyanates such as 1,4-tetramethylene diisocyanate, 2-methylpentamethylene 1,5-diisocyanate, 1,6-hexamethylene diisocyanate (HDI), 2,2,4- and 2,4,4-trimethyl-1,6-hexamethylene diisocyanate (TMDI), 1,10-decamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, lysine diisocyanate and lysine ester diisocyanate, cyclohexane-1,3- and 1,4-diisocyanate, 1-methyl-2,4- and 2,6-diisocyanatocyclohexane and any desired mixtures of these isomers (HTDI or H6TDI), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (= isophorone diisocyanate or IPDI), perhydro-2,4'- and 4,4'-diphenylmethane diisocyanate (HMDI or H12MDI), 1,4-diisocyanato-2,2,6-trimethylcyclohexane (TMCDI), 1,3- and 1,4-bis(isocyanatomethyl)cyclohexane, m- and p-xyylene diisocyanate (m- and p-XDI), m- and p-tetramethyl-1,3-xylene diisocyanate and -1,4-xylene diisocyanate (m- and p-TMXDI), bis(1-isocyanato-1-methylethyl)naphthalene, dimer and trimer fatty acid isocyanates such as 3,6-bis(9-isocyanatononyl)-4,5-di-(1-heptenyl)cyclohexane (dimeryl diisocyanate) and $\alpha,\alpha,\alpha',\alpha':\alpha''$-hexamethyl-1,3,5-mesitylene triisocyanate.

In a further embodiment the polyisocyanate (PI) is an oligomeric polyisocyanate (PI-O) of the above mentioned monomeric polyisocyanates (PI-M). Suitable oligomers of a monomeric diisocyanate include more particularly the oligomers of HDI, IPDI and TDI. In practice, such oligomers usually constitute mixtures of substances having different degrees of
oligomerization and/or chemical structures. They preferably have an average NCO functionality of 2.1 to 4.0 and contain, more particularly isocyanurate groups, iminooxadiazinedione groups, uretdione groups, urethane groups, biuret groups, allophanate groups, carbodiimide groups, uretonimine groups or oxadiazinetrione groups. They preferably have a low monomeric diisocyanate content. Commercially available products are, more particularly, HDI biurets, for example Desmodur® N 100 and Desmodur® N 3200 (from Bayer), Tolonate® HDB and Tolonate® HDB-LV (from Perstorp) and also Duranate® 24A-1 00 (from Asahi Kasei); HDI isocyanurates, examples being Desmodur® N 3300, Desmodur® N 3600 and Desmodur® N 3790 BA (from Bayer), Desmodur® N 3390 BA (from Bayer), Tolonate® HDT, Tolonate® HDT-LV and Tolonate® HDT-LV2 (from Perstorp), (Duranate® TPA-1 00 and Duranate® THA-100 (from Asahi Kasei) and also Coronate® HX (from Nippon Polyurethane); HDI uretdiones, an example being Desmodur® N 3400 (from Bayer); HDI iminooxadiazinediones, an example being Desmodur® XP 241 0 (from Bayer); HDI allophanates, an example being Desmodur® VP LS 2 102 (from Bayer); IPDI isocyanurates, examples being Desmodur® Z 4470 (from Bayer) and Vestanat® T 1890/1 00 (from Evonik); TDI oligomers, an example being Desmodur® IL (from Bayer); and also mixed isocyanurates based on TDI/HDI, as for example Desmodur® HL (from Bayer).

In a further embodiment the polyisocyanate (PI) is a polyurethane polymer (PUP) containing isocyanate groups.

The term "polyurethane polymer" encompasses all polymers which are prepared by the process known as the diisocyanate polyaddition process. This also includes those polymers which are entirely or virtually free from urethane groups. Examples of polyurethane polymers are polyether-polyurethanes, polyester-polyurethanes, polyether-polyureas, polyureas, polyester-polyureas, polyisocyanurates and polycarbodiimides.

One suitable polyurethane polymer (PUP) is obtainable more particularly from the reaction of at least one polyol with at least one polyisocyanate, particularly with a monomeric polyisocyanates (PI-M) and/or an oligomeric polyisocyanate (PI-O) being both mentioned above.
This reaction may involve the polyol and the polyisocyanate being reacted by customary methods, at temperatures, for example of 50°C to 100°C, optionally with accompanying use of suitable catalysts, the amount of the polyisocyanate being such that its isocyanate groups are present in a stoichiometric excess in relation to the hydroxyl groups of the polyol. The amount of the polyisocyanate is advantageously such that an NCO/OH ratio of 1.3 to 5, more particularly of 1.5 to 3, is observed. The "NCO/OH ratio" means the ratio of the number of isocyanate groups used to the number of hydroxyl groups used. After the reaction of all of the hydroxyl groups of the polyol, the polyurethane polymer (PUP) preferably retains a free isocyanate group content of 0.5 to 15% by weight, more preferably of 0.5 to 10% by weight.

The polyols which can be used for preparing a polyurethane polymer (PUP) include, for example, the following commercially customary polyol or mixtures thereof:

- polyoxyalkylene polyols, also called polyether polyols or oligoetherols, which are polymerization products of ethylene oxide, 1,2-propylene oxide, 1,2- or 2,3-butylene oxide, oxetane, tetrahydrofuran or mixtures thereof, optionally polymerized by means of a starter molecule having two or more active hydrogen atoms, such as, for example, water, ammonia or compounds having two or more OH or NH groups, such as, for example, 1,2-ethanediol, 1,2- and 1,3-propanediol, neopentylglycol, diethylene glycol, triethylene glycol, the isomeric dipropylene glycols and tripropylene glycols, the isomeric butanediols, pentanediols, hexanediols, heptanediols, octanediols, nonanediols, decanediols, undecanediols, 1,3- and 1,4-cyclohexanedi- dimethanol, bisphenol A, hydrogenated bisphenol A, 1,1,1-trimethylethylene, 1,1,1-trimethylolpropane, glycerol, aniline, and also mixtures of the aforementioned compounds. Use may be made not only of polyoxyalkylene polyols which have a low degree of unsaturation (measured in accordance with ASTM D-2849-69 and expressed in milliequivalents of unsaturation per gram of polyol (meq/g)), prepared, for example, by means of what are called double metal cyanide complex catalysts (DMC catalysts), but also of polyoxyalkylene polyols having a higher degree of unsaturation, prepared,
for example, by means of anionic catalysts such as NaOH, KOH, CsOH or alkali metal alkoxides.

Particularly suitable are polyoxyalkylene diols or polyoxyalkylene triols, more particularly polyoxyethylene and polyoxypropylene diols and triols.

Especially suitable are polyoxyalkylene diols and triols having a degree of unsaturation of less than 0.02 meq/g and having a molecular weight in the range of 1000 - 30 000 g/mol, and also polyoxypropylene diols and triols having a molecular weight of 400 - 8000 g/mol.

Likewise particularly suitable are what are called ethylene oxide-terminated (EO-end capped", ethylene oxide-end capped) polyoxypropylene polyols.

The latter are special polyoxypropylene-polyoxyethylene polyols which are obtained, for example, by further alkoxylation pure polyoxypropylene polyols, more particularly polyoxypropylene diols and triols, with ethylene oxide after the end of the polypropoxylation reaction, and as a result contain primary hydroxyl groups.

- Styrene-acrylonitrile or acrylonitrile-methyl methacrylate-grafted polyether polyols.
- Polyester polyols, also called oligoesters, prepared for example from dihydric to trihydric alcohols such as, for example, 1,2-ethanediol, diethylene glycol, 1,2-propanediol, dipropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentylglycol, glycerol, 1,1,1-trimethylol propane or mixtures of the aforementioned alcohols with organic dicarboxylic acids or their anhydrides or esters such as, for example, succinic acid, glutaric acid, adipic acid, suberic acid, sebacic acid, dodecanedicarboxylic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid and hexahydrophthalic acid or mixtures of the aforementioned acids, and also polyester polyols from lactones such as ε-caprolactone, for example.
- Polycarbonate polyols, of the kind obtainable by reaction, for example, of the abovementioned alcohols - those used to construct the polyester polyols - with dialkyl carbonates, diaryl carbonates or phosgene.
- Block copolymers which carry at least two hydroxyl groups and which contain at least two different blocks with polyether, polyester and/or polycarbonate structure of the type described above.
- Polyacrylate polyols and polymethacrylate polyols.
- Polyhydrocarbon polyols, also called oligohydrocarbonols, such as, for example, polyhydroxy-functional ethylene-propylene, ethylene-butylene or ethylene-propylene-diene copolymers, of the kind produced, for example, by the company Kraton Polymers, or polyhydroxy-functional copolymers of dienes such as 1,3-butadiene or diene mixtures and vinyl monomers such as styrene, acrylonitrile or isobutylene, or polyhydroxy-functional polybutadiene polyols, such as, for example, those which are prepared by copolymerization of 1,3-butadiene and allyl alcohol and which may also have been hydrogenated.
- Polyhydroxy-functional acrylonitrile/butadiene copolymers, of the kind preparable, for example, from epoxides or amino alcohols and carboxyl-terminated acrylonitrile/butadiene copolymers (available commercially under the name Hypro® CTBN from Hanse Chemie).

These stated polyols preferably have an average molecular weight of 250 - 30 000 g/mol, more particularly of 400 - 20 000 g/mol, and preferably have an average OH functionality in the range from 1.6 to 3.

Preferred polyols are polyether, polyester, polycarbonate and polyacrylate polyols, preferably diols and triols. Particularly preferred are polyether polyols, more particularly polyoxypropylene polyols and polyoxypropylene-polyoxyethylene polyols.

The polyisocyanates (PI) are preferred to be oligomeric polyisocyanate (PI-O) or monomeric polyisocyanates (PI-M).

Preferably the polyisocyanate (PI) has a molecular weight of less than 700g/mol, particularly of between 400 and 670 g/mol.

More preferably the polyisocyanate (PI) is selected from the group consisting of 1,6-hexamethylene diisocyanate (HDI), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate or IPDI),
2,4-toluene diisocyanate, 2,6-toluene diisocyanate and the isocyanurates or biurets or uretdiones thereof.

The second (C2) may also comprise further ingredients which are principally known to the person skilled in the art in the field of 2 component polyurethanes. Particularly useful additional ingredients of the second pack are plasticizers, solvents, inorganic and organic fillers, such as catalysts, particularly for catalyzing the NCO/OH reaction, rheology modifiers, driers, adhesion promoters, stabilizers against heat, light and UV radiation, flame retardants, biocides, pigments or surface-active substances as for example wetting agents, flow control agents, de-aerating agents or defoamers.

It is advantageous to ensure that such additional ingredients do not adversely affect the stability of the second pack (C2) in storage. This means that these ingredients not give rise to any significant extent, in the course of storage, to the reactions that lead to reactions, particularly to crosslinking. More particularly this implies that all of these additions should not contain any water, or at most only traces of water. It may, therefore, be sensible to carry out chemical or physical drying of certain additions prior to their incorporation into the composition by mixing.

Therefore, these optional ingredients should particularly not react with the other ingredients in said pack, particularly not with the polyisocyanate, or trigger some reaction of ingredients being present in the first pack.

As it is preferred for the two part polyurethane composition to have low content of VOC (Volatile Organic Compounds) it is preferred that the first and/or the second pack has a very low content of, preferably no at all, solvent as additional ingredient in the two-part polyurethane composition.

The content of first pack and the second pack (C2) are filled and stored in individual compartments, respectively packaging, to yield first pack (C1), respectively second pack (C2). Such compartments, respectively packaging, are particularly in form of drums, pails, hobbocks, cartridge, bags, pouch, bucket or unipacks. The packaging, respectively so formed packs packs may also be attached to each others, typically in the form of twin cartridges (side-by-
side arrangement) or cartridge-in-cartridge (co-central arrangement), which are usual packs, respectively packaging, for two part compositions.

The first pack (C1) and the second pack (C2) as described are prepared separately from one another, and at least the second pack (C2) in the absence of moisture. The two packs (components) are stable in storage separately from one another at room temperature or slightly elevated temperature. That is, they can each be kept in a suitable packaging or facility, as, for example, in a drum, a hobbock, a pouch, a bucket or a cartridge, for a period of several months up to a year or more prior to their application, without undergoing alteration in their respective properties to any extent relevant for their utility.

For using the two-part polyurethane composition the content of the first pack (C1) and the content of the second pack (C2) of the two-part polyurethane composition as disclosed above need to be mixed.

The mixing ratio between the two packs (C1 and C2) is preferably selected in such a ratio, that the amount of polyisocyanate (PI) is present in such an amount that the ratio of number hydroxyl groups being present in the first pack (C1) to the number of isocyanate groups in the second pack (C2) is a value between 0.9 and 1.1. This assures a fairly complete curing of the mixed two-part polyurethane composition.

The disclosed two-part polyurethane composition can be broadly used, particularly as adhesive, sealant, primer, coating, paint or floor coating.

In a further aspect the present invention relates, to a coating which is obtained by a procedure comprising the steps:

i) the mixing of the content of the first pack (C1) and the content of the second pack (C2) of a two-part polyurethane composition as described above in detail, resulting in a mixed two-part polyurethane composition;

ii) applying the mixed two-part polyurethane composition onto a substrate (S);

iii) curing of the mixed two-part polyurethane composition.
The mixing of the two components may be done in one embodiment by metering the amount of content of the first and second pack (C1 and C2) and mixing the two components by means application of a stirrer, a static or a dynamic mixer or by twin-feed spray technique in order to achieve a mixing quality being preferred as high as possible. The metering can be done either manually or automatically such as a metering pump or by coupled movement of pistons such as realized in a known twin cartridge system.

Mixing may take place continuously or batchwise. If mixing takes place prior to application, it must be ensured that the time which elapses between the mixing of the two components (C1 and C2) and the application is not too great, since otherwise there may be defects, such as a delayed or incomplete curing or incomplete development of adhesion to the surface of the solid, for example.

It has been observed that the mixed two-part polyurethane composition may exhibit relatively low viscosity in comparison with analogous formulations using known polyols other than the hyperbranched copolymer (HBC) having pending OH groups being described above in detail. This allows on the one hand either to achieve better mixing quality, easier application or on the other hand to achieve a higher amount of filler to be used which results in a cheaper formulation. Finally lower viscosity also allows better sprayability and better film quality.

The mixed two-part polyurethane composition can be applied manually or automatically e.g. by means of a robot. The application of the two-part polyurethane composition can occur for example in the form of a spray, of a bead, by pouring, brushing, coating, spreading, scraping, wiping or dipping.

In the above procedure, suitable substrates (S) are, for example, inorganic substrates such as glass, glass ceramic, concrete, mortar, brick, tile, plaster, and natural stones such as granite or marble; metals or alloys such as aluminum, steel, nonferrous metals, galvanized metals; organic substrates such as leather, fabrics, paper, wood, resin-bound wood-based materials, resin-textile composites, plastics such as polyvinyl chloride (unplasticized and plasticized PVC), acrylonitrile-butadiene-styrene copolymers (ABS), SMC
(sheet molding composites), polycarbonate (PC), polyamide (PA), polyesters, PMMA, polyesters, epoxy resins, polyurethanes (PUR), polyoxymethylene (POM), polyolefins (PO), especially polyethylene (PE) or polypropylene (PP) surface-treated by plasma, corona or flames, ethylene/propylene copolymers (EPM) and ethylene/propylene-diene terpolymers (EPDM); coated substrates such as powder-coated metals or alloys; and also inks and paints, more particularly automotive paints.

The substrates may where necessary be pretreated prior to application of the composition. Such pretreatments include in particular, physical and/or chemical cleaning processes, such as abrading, sandblasting, brushing or the like, for example, or treatment with cleaners or solvents or the application of an adhesion promoter, an adhesion-promoter solution or a primer.

During and after application, the composition begins to cure. It has been observed that the two-part polyurethane composition may cure very fast particularly under heated conditions in comparison to linear acrylic polyol systems.

The two-part polyurethane composition has a series of different advantages such as combining low viscosity, long pot life, fast cure, advantageous adhesion properties, excellent weathering, UV and chemical resistance. Furthermore, it forms excellent films. The visual aspect of those films such as colour and gloss combined with good adhesion and scratch resistance and exceptional flexibility are very advantageous and particular important when using a two-part polyurethane composition for preparation of coatings.

Due to the low viscous properties of the hyperbranched copolymer (HBC) having pending OH groups the present invention also relates to the use of the hyperbranched copolymer (HBC) having pending OH groups of a two-part polyurethane composition as described above for a as a non-crystallising curing agent for isocyanates. It is very advantages that such curing agents are not crystalline as this increases the quality of mixing and the rate of curing.
Furthermore, the present invention relates also to a method of reacting the hyperbranched copolymer (HBC) having pending OH groups of a two-part composition as described above with at least one polyisocyanate characterized in that the hyperbranched copolymer (HBC) is brought in physical contact with the polyisocyanate.

This contacting might be for example a simple or thorough mixing of the hyperbranched copolymer (HBC) and the polyisocyanate. In a specific embodiment where the hyperbranched copolymer (HBC), respectively a composition thereof, is applied in a small layer on one substrate surface, and where the polyisocyanate, respectively a composition thereof, is applied on another substrate surface, a reaction can occur between the hyperbranched copolymer (HBC) and the polyisocyanate by simply contacting the two surfaces with each other.

In a further embodiment the reaction between the hyperbranched copolymer (HBC) having pending OH and at least one polyisocyanate leads to a reaction product.

Depending on the ratio between the hydroxyl groups and the isocyanate groups the reaction product either exhibits some hydroxyl groups or some isocyanate groups.

If the reaction between the hyperbranched copolymer (HBC) having pending OH groups with at least one polyisocyanate is done in a such a ratio that the number of NCO groups of the polyisocyanate the number of OH groups of the hyperbranched copolymer (HBC) is < 1, particularly less than 0.5, preferably of 0.4 - 0.1, a relatively low viscous (despite the very high molecular weight) polyol having a very high OH functionality is obtained, basically being two hyperbranched polyol molecules being bridged by the polyisocyanate. Such polyols are suited well for getting polyurethanes of very high mechanical strength, particularly high stiffness and high glass transition temperatures.

If the reaction between the hyperbranched copolymer (HBC) having pending OH groups with at least one polyisocyanate is done in a such a ratio
that the number of NCO groups of the polyisocyanate the number of OH
groups of the hyperbranched copolymer (HBC) is $> 1$, a reaction product
having pending NCO groups (HBC-NCO) is obtained. Such reaction products
represent a further aspect of the present invention. Particularly preferred are
such polymers, in which all of the OH groups of the hyperbranched copolymer
(HBC) are reacted by the polyisocyanates. However, it is preferred that the
polyisocyanate does not crosslink individual hyperbranched copolymers which
would lead fast to very high molecular weight.

Such a reaction product having pending NCO groups (HBC-NCO)

10 represent low viscous polyisocyanates having a very high NCO functionality
and hence is suited very well as efficient crosslinker in polyurethane systems.
Particularly, they yield polyurethane composition of extreme high mechanical
properties, particularly high stiffness and high glass transition temperatures.
Very unique properties are obtained in case if such a reaction product having
pending NCO groups (HBC-NCO) is combined with polyurethane polymer

15 (PUP) containing isocyanate groups which have been described above. In
such system a synergistic effect of the properties of the elastic part stemming
from the polyurethane (PUP) and the stiff part stemming from the reaction
product (HBC-NCO) can be achieved. Particularly useful are these reaction
products having pending NCO groups (HBC-NCO) in the field of coatings,
particularly powder coatings.
Examples

Raw materials

<table>
<thead>
<tr>
<th>Raw material</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl methacrylate, ≥99.9% (‘MMA’)</td>
<td>Lucite</td>
</tr>
<tr>
<td>n-Butyl methacrylate, ≥99.5% (‘n-BMA’)</td>
<td>Evonik</td>
</tr>
<tr>
<td>Hydroxypropyl methacrylate, ≥98% (‘HPMA’)</td>
<td>Evonik</td>
</tr>
<tr>
<td>Ethylene glycol dimethacrylate, ≥99% (‘EGDMA’)</td>
<td>Evonik</td>
</tr>
<tr>
<td>2-Mercapto ethanol, ≥99%</td>
<td>Aldrich</td>
</tr>
<tr>
<td>n-butyl acetate, ≥99.5% (‘BuAc’))</td>
<td>Celanese</td>
</tr>
<tr>
<td>2,2’-azobis(isobutrylonitrile) (AIBN), Vazo 64</td>
<td>DuPont</td>
</tr>
<tr>
<td>Cobalt(II) acetate tetrahydrate, AS reagent, ≥98.0%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Dimethylglyoxime, ACS reagent, ≥99%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Diethyl ether, ACS reagent, anhydrous, 99.7%</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Boron trifluoride diethyl etherate</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>Joncryl® 922</td>
<td>Johnson Polymer</td>
</tr>
<tr>
<td>G-Cure® 192</td>
<td>Cognis</td>
</tr>
<tr>
<td>Synocure 852 BA80 (‘Synocure 852’)</td>
<td>Cray Valley</td>
</tr>
<tr>
<td>n-butyl acetate</td>
<td></td>
</tr>
<tr>
<td>Tinuvin® 1130 (UV absorber)</td>
<td>BASF</td>
</tr>
<tr>
<td>Tinuvin® 292 (hindered amine light stabilizer, HALS)</td>
<td>BASF</td>
</tr>
<tr>
<td>10% Dibutyl tin dilaurate (DBTL) in BuAc</td>
<td></td>
</tr>
<tr>
<td>Desmodur® N 3390 BA (Aliphatic polyisocyanate (HDI trimer) (90% in BuAc)</td>
<td>Bayer Material Science</td>
</tr>
</tbody>
</table>

Table 1. Raw materials (were used as received without further treatment)

Preparation of Hyperbranched polvol using 2-mercaptoethanol as chain transfer catalyst: **HP-Ref.**

3.380 kg (3.380 mole) of methyl methacrylate, 1.020 kg (7.075 mole) of hydroxypropyl methacrylate, 1.000 kg (7.032 mole) n-butyl methacrylate, 0.800 kg (4.040 mole) of ethylene glycol dimethacrylate, 0.840 kg (10.769 mole) of 2-mercaptoethanol, 0.500 kg of n-butyl acetate and 0.160 kg (0.974 mole) 2,2’-
azobis(isobutryronitrile) were charged into a 10-litre preparation vessel and the mixture de-gassed by bubbling nitrogen through for 30 minutes with gentle agitation. 1.500 kg of n-butyl acetate was charged into a 10-litre reaction vessel equipped with a condenser, a 4-bladed propeller stirrer and N₂ inlet and heated to above 80°C. With agitation, the monomer mixture made in the preparation vessel was charged into the reaction vessel using a peristaltic pump over 45 minutes during which the temperature was maintained between 80 and 150°C. The mixture was stirred for a further 2 hours during which the temperature was maintained above 80°C. A mixture of 0.424 kg (4.24 mole) of MMA, 0.285 kg (1.9768 mole) of HPMA, 0.035 kg (0.246 mole) of n-BMA, 0.032 kg (0.162 mole) of EGDMA and 0.200 kg of n-butyl acetate made previously was then charged into the reaction vessel at 80°C at which the reaction mixture was stirred for a further hour. The reaction mixture was allowed to cool to 60°C and a clear, viscous product obtained by filtering through a 50 micron bag. The viscosity at 20°C was 8200 mPa*s (cP) with a solids content of 78-82%.

Preparation of cobalt (II) complex: **CC-1**

The synthesis has been made according to A.Bakac et al., *J. Am. Chem. Soc.* 1984, 106, 5197-5202:

To a 1 litre flask was added 40 grams of cobalt(II) acetate tetrahydrate and 600 ml of anhydrous diethyl ether. The mixture was stirred and 40 grams of dimethylglyoxime was added. The mixture was refluxed during stirring for two hours followed by the drop wise addition of boron trifluoride diethyl etherate. The mixture was stirred under refluxing overnight. The product was filtered and washed with 20 ml of cold de-ionised water three times and dried under vacuum at room temperature. 36.5 gram of bis(borondifluoro-dimethylglyoximate) cobaltate (II) have been obtained and has been abbreviated as **CC-1** for further use.

Preparation of hyperbranched polvol using cobalt (II) complex **CC-1** as chain transfer catalyst: **HPC-1**

Into a 350-litre reaction vessel was charged 60.00 kg of n-butyl acetate. With slow agitation nitrogen was bubbled through the liquid at 2 litre /
minute for 30 minutes. The solvent was then heated and maintained at above 80°C. Into the header tank was charged 72.00 kg of hydroxypropyl methacrylate, 8.00 kg of ethylene glycol dimethacrylate, 10.00 kg of n-butyl acetate, 40.00 kg of n-butyl methacrylate, 80.00 kg of methyl methacrylate and 3.00 kg of AIBN. After the AIBN was fully dissolved, nitrogen was passed through the solution at 2 litre/minute for 30 minutes. A solution of 12 g of the above cobalt (II) complex CC-1 in 2 litre acetone was added into the monomer solution and was stirred until the solution was homogenous. The monomer solution was charged over 45 minutes into the reaction vessel under agitation whilst the temperature was maintained at between 80-150°C. The mixture was stirred for a further two hours and the reaction temperature maintained above 80°C. After the reaction, 20 litres of solvent was distilled out under reduced pressure. The product was filtered through a 50micron bag to give a clear pale viscous liquid having the solids of 78%, a viscosity of 12000 mPa*s(cP) at 20°C and an OH content of 4.2%.

Preparation of two-part polyurethane compositions

Two part polyurethane compositions have been prepared in the following manner using the ingredients in the amounts of table 2.

The first part (component) has been formed by mixing the polyol into the solvent followed by adding the Tinuvin® additives and the tin catalyst. Catalyst levels are slightly different in order to make pot life and cure rates comparable.

The Desmodur® N 3390 BA was used as second part (component).

To the first part 33.4 g of the second part was added and mixed by propeller stirrer to yield a total amount of mixed composition indicated in table 2.

The example Ref.1 is a reference example using a hyperbranched polyol using a mercapto compound as chain transfer catalyst. The reference examples Ref.2 to Ref.5 all use different traditional acrylic polyols being commercially available. All acrylic polyols are at 80% solids in butyl acetate.
Table 2. Two-part compositions.

Properties of the two-part compositions

Viscosity:

The viscosity of the compositions was characterized directly after mixed by the determination of the flow time by use of flow cups. For the present test BS 3900 A6 No. 4 flow cups (according to ISO 2431) were used at room temperature for the mixed compositions and the flow time indicated in seconds in table 3.

Pot Life:

The initial viscosity (η₀) was measured (in seconds) using the above flow cup method directly after mixing. Further measurements of viscosity (ηₜ) were undertaken after different times (tₜ) after mixing. As pot life that time was identified for which the viscosity (ηₜ) is the double (in seconds) of the initial viscosity (η₀). Long pot life is always useful for formulators for the convenience of application.
Hardness:

Films of mixed compositions were casted (100 micron wet film thickness) using a 100 micron draw down bar (Sheen Wire Bar Coater 1120/25/1 00) on a Q-Panel (A-36 aluminium panels (76x1 52x0.625 mm) supplied by Q-Lab). The solvent was allowed to evaporate in a fume cupboard for 30 minutes before being cured in the oven (80°C) for 5 minutes, resp. 30 minutes, or in air (at room temperature) for 6 hours, resp. 24 hours, resp. 7 days. The hardness of the films was followed using a Persoz pendulum hardness test equipment. A measure for the hardness was hence the time (in seconds) of swinging amplitude to decrease from 12° to 4°.

UV-Stability:

The UV-stability was assessed by means of QUV-A weathering stability test method. For the test were used Q-panels coated with the respective PU films as described above (Hardness). The panels were allowed to cure for at least 21 days before subjecting to QUV test.

All two-part compositions were subjected to accelerated weathering tests. The ASTM G154-04 cycle 3 was used in the accelerated QUV-A weathering stability test. The cycle involved an 8-hour UV radiation at 70°C and a 4-hour water condensation at 50°C.

After 1000 h testing the samples were assessed in view of colouring. Yellowing is a measure for UV-instability. Furthermore, the gloss was measured before ("Original Gloss") and after the 1000 h QUA-V test exposure. The retension of gloss (in %) is taken as a measure of UV-stability. The gloss of the films has been measured with An Elcometer® 407 Statistical Gloss-meter. The gloss was measured at three angles of reflection 20°, 60° and 85°. The higher the retension the better is the UV-stability.

\[ \text{Retension of gloss} = \frac{\text{Gloss after 1000 h QUV-A}}{\text{Original Gloss}} \]

The values measured as discussed above are compiled in table 3.
Flexibility and adhesion:

The flexibility and adhesion was measured using the Conical bending test in the following matter: The Q-Panels coated by the fully cured polyurethane film as described above (Hardness) were bent to 120° and the film around the bending edge was observed. If a peeling of the film has been detected the adhesion and flexibility were both rated "poor". If cracks of the film have been detected the flexibility has been rated "poor". If no peeling off the film nor cracks have been observed adhesion and flexibility were rated "good".

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>Ref. 1</th>
<th>Ref. 2</th>
<th>Ref. 3</th>
<th>Ref. 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity [s]</td>
<td>37</td>
<td>33</td>
<td>45</td>
<td>50</td>
<td>55</td>
</tr>
<tr>
<td>Pot life [min.]</td>
<td>60</td>
<td>80</td>
<td>45</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td><strong>Hardness</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardness 5 min at 80°C [s]</td>
<td>31</td>
<td>153</td>
<td>13</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Hardness 30 min at 80°C [s]</td>
<td>288</td>
<td>280</td>
<td>220</td>
<td>286</td>
<td>177</td>
</tr>
<tr>
<td>Hardness 6 hr at 23°C [s]</td>
<td>29</td>
<td>61</td>
<td>19</td>
<td>20</td>
<td>18</td>
</tr>
<tr>
<td>Hardness 24 hr at 23°C [s]</td>
<td>136</td>
<td>132</td>
<td>190</td>
<td>232</td>
<td>142</td>
</tr>
<tr>
<td>Hardness 7 day at 23°C [s]</td>
<td>271</td>
<td>285</td>
<td>256</td>
<td>296</td>
<td>320</td>
</tr>
<tr>
<td><strong>1000h QUV Retention of gloss</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gloss measured at 20° [%]</td>
<td>98</td>
<td>56</td>
<td>68</td>
<td>70</td>
<td>80</td>
</tr>
<tr>
<td>Gloss measured at 60° [%]</td>
<td>98</td>
<td>63</td>
<td>81</td>
<td>80</td>
<td>96</td>
</tr>
<tr>
<td>Gloss measured at 85° [%]</td>
<td>98</td>
<td>67</td>
<td>94</td>
<td>98</td>
<td>96</td>
</tr>
<tr>
<td><strong>Colour</strong></td>
<td>None</td>
<td>None</td>
<td>Yellow</td>
<td>Yellow</td>
<td>Yellow</td>
</tr>
<tr>
<td><strong>Adhesion</strong></td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
<td>Poor</td>
<td>Poor</td>
</tr>
<tr>
<td><strong>Flexibility</strong></td>
<td>Good</td>
<td>Good</td>
<td>Poor</td>
<td>Poor</td>
<td>Poor</td>
</tr>
</tbody>
</table>

Table 3. Properties of two-part compositions.

The results in table 3 show that example 1 and Ref.1 had the lowest viscosities of all the systems tested. As discussed before, low viscosity is always an advantage from both application and low VOC points of view.

It can be also seen that Ref.1 formulation had the longest pot life whilst the 1 had the second longest pot life. Considering the lower starting viscosities,
in case of example 1 and Ref. 1, the time until they have reached the same viscosity level than the other examples is even longer, resulting in a much longer workability.

The results from table 3 also show that the experiment 1 has a much higher flexibility and adhesion that those examples formulated with traditional polyols (Ref. 2 - Ref. 4).

The values of hardness show that the examples 1 and Ref. 1 -despite the extended pot-life - develop very fast a high hardness that as well at 80°C (Hardness 5min at 80°C) as at room temperature (Hardness 6 hr at 23°C) as compared as to the composition using the conventional polyols. The hardness obtained on long term curing is, however, more or less at a comparable level.

It is also visible from table 3, that the examples 1 and Ref. 1 remain clear and do not exhibit yellowing. However, in comparing the examples 1 and Ref. 1 it is clearly visible from the data that the example Ref. 1, i.e. the formulation based on the hyperbranched polyol prepared by means of mercapto compound as chain transfer catalyst, exhibits for all angles measured much lower gloss retention values as compared to the example according to the invention (1) which is a clear measure that example Ref. 1 has much lower UV resistance than example 1.
Patent Claims

1. Two-part polyurethane composition consisting of a first pack (C1) and of a second pack (C2), wherein
   the first pack (C1) comprises
   at least one hyperbranched copolymer (HBC) having pending OH groups and which is prepared from at least
   a) one or more monomer(s) (M2) having at least two unsaturated C-C bonds
   b) one or more monomer(s) (MH) having one unsaturated C-C bonds
   and one hydroxyl group
   in the presence of a cobalt (II) complex (CC)
   the second pack (C2) comprises
   at least one polyisocyanate (PI).

2. Two-part polyurethane composition according to claim 1, characterized in that the cobalt (II) complex (CC) is a bis(borondifluorodimethylglyoximate) cobaltate (II) complex.

3. Two-part polyurethane composition according to claim 1 or 2,
   characterized in that the hyperbranched copolymer (HBC) is prepared from
   a') one or more monomer(s) having at least two unsaturated C-C bonds (M2);
   b') one or more monomer(s) having one unsaturated C-C bonds (MH)
   and one hydroxyl group;
   c') one or more monomer(s) having one unsaturated C-C bonds (M1)
   in the presence of a non-peroxide initiator (IN) and the cobalt (II) complex (CC).

4. Two-part polyurethane composition according to any one of the preceding claims, characterized in that the hyperbranched copolymer (HBC) is prepared from
   a'') one or more di(meth)acrylate(s) (M2');
   b'') one or more hydroxyalkyl(meth)acrylate(s) (MH') and
c") one or more alkyl(meth)acrylate(s) (M1') in the presence of an azo initiator, particularly 2,2-azobis-(isobutyronitrile), and the cobalt (II) complex (CC).

5. Two-part polyurethane composition according to claim 4, characterized in that the hyperbranched copolymer (HBC) is prepared from

1 - 20 % by weight, particularly 1.5 - 15 % by weight, of di(meth)acrylate (M2'), related to the weight sum of di(meth)acrylate (M2') and hydroxyalkyl(meth)acrylate(s) (MH') and alkyl(meth)acrylate(s) (MV);

10 10 - 45 % by weight, particularly 15 - 35 % by weight, of hydroxyalkyl(meth)acrylate(s) (MH'), related to the weight sum of di(meth)acrylate (M2') and hydroxyalkyl(meth)acrylate(s) (MH') and alkyl(meth)acrylate(s) (MV)

and

15 30 - 80 % by weight, particularly 60 - 75 % by weight, of alkyl(meth)acrylate(s) (MV), related to the weight sum of di(meth)acrylate (M2') and hydroxyalkyl(meth)acrylate(s) (MH') and alkyl(meth)acrylate(s) (MV);

in the presence of an azo initiator, particularly 2,2-azobis-(isobutyronitrile), and the cobalt (II) complex (CC).

6. Two-part polyurethane composition according to claim 4 or 5, characterized in that the di(meth)acrylate is an (poly)alkylene or (poly)oxyalkylene bridged di(meth)acrylate.

7. Two-part polyurethane composition according to claim 4 or 5 or 6, characterized in that the di(meth)acrylate is of formula (l-a) or (l-b)

\[
\begin{align*}
\text{(I-a)} & \quad \text{O} - \text{R}^2 - \text{O} - \text{R}^1 \\
\end{align*}
\]
wherein $R^1$ is H or a methyl group, preferably a methyl group;
$R^2$ is a linear or branched alkylene group with 2 to 30 carbon atoms, particularly 2 to 15 carbon atoms, preferably an ethylene, propylene, isopropylene or butylene group;
$R^3$ is a linear or branched alkylene group with 2 to 6 carbon atoms and $n$ is an integer from 2 to 6.

8. Two-part polyurethane composition according to anyone of the claims 3 to 7, characterized in that the hydroxyalkyl(meth)acrylate has the formula (II).

![Formula II](image)

wherein $R^1$ is H or a methyl group, preferably a methyl group, and $R^4$ is a linear or branched alkylene group of 1 to 10 carbon atoms, particularly a methylene or ethylene or propylene or butylene group.

9. Two-part polyurethane composition according to any one of the preceding claims, characterized in that the cobalt (II) complex (CC) is used in the preparation of the hyperbranched copolymer (HBC) in a concentration of less than 1 % by weight, particularly less than 0.5 % by weight, preferably of 0.001 to 0.1 % by weight, relative to the weight of the monomers having unsaturated C-C bonds.

10. Two-part polyurethane composition according to any one of the preceding claims, characterized in that the polyisocyanate (PI) has a molecular weight of less than 700g/mol, particularly of between 400 and 670 g/mol.
11. Two-part polyurethane composition according to any one of the preceding claims, characterized in that the polyisocyanate (PI) is selected from the group consisting of 1,6-hexamethylene diisocyanate (HDI), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate or IPDI), 2,4-toluene diisocyanate, 2,6-toluene diisocyanate and the isocyanurates or biurets or uretdiones thereof.

12. Two-part polyurethane composition according to any one of the preceding claims, characterized in that the amount of polyisocyanate (PI) is present in such an amount that the ratio of number hydroxyl groups being present in the first pack (C1) to the number of isocyanate groups in the second pack (C2) is a value between 0.9 and 1.1.

13. A Coating obtained by a procedure of comprising the steps:

i) the mixing of the content of the first pack (C1) and the content of the second pack (C2) of a two-part polyurethane composition according to any one of the preceding claims 1 to 12, resulting in a mixed two-part polyurethane composition;

ii) applying the mixed two-part polyurethane composition onto a substrate (S);

iii) curing of the mixed two-part polyurethane composition.

14. Use of the hyperbranched copolymer (HBC) having pending OH groups of a two-part polyurethane composition according to any one of the claims 1 to 12 as a non-crystallising curing agent for isocyanates.

15. Method of reacting the hyperbranched copolymer (HBC) having pending OH groups according to a two-part composition according to any one of the claims 1 to 12 with at least one polyisocyanate characterized in that the hyperbranched copolymer (HBC) is brought in physical contact with the polyisocyanate.
16. Reaction product having pending NCO groups obtained by reacting the hyperbranched copolymer (HBC) having pending OH groups according to a two-part composition according to any one of the claims 1 to 12 with at least one polyisocyanate in a such a ratio that the number of NCO groups of the polyisocyanate the number of OH groups of the hyperbranched copolymer (HBC) is > 1, particularly more than 2, preferably of 2.5 - 10.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C08G18/62 C08F2/38

According to International Patent Classification (IPC) of both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C08G C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<th>Category</th>
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<td>US 5 985 998 A (SOMMERFELD EUGENE G [US] ET AL) 16 November 1999 (1999-11-16)</td>
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Further documents are listed in the continuation of Box C. [X] See patent family annex.

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

Date of the actual completion of the international search: 25 January 2012

Date of mailing of the international search report: 31/01/2012

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer: Bezard, Stephane
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