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 (54) Title: ADHESIVE SYSTEM FOR SILICONES

(57) **Abrégé/Abstract:**

The invention relates to a kit comprising the following: a) at least one resolubilizable (co)polymer, b) at least one adhesive for silicones, optionally c) a base body and optionally, d) a silicone compound. The invention also relates to the use of this kit for producing an impression tray.



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<p>(54) Title: ADHESIVE SYSTEM FOR SILICONES</p> <p>(54) Bezeichnung: ADHESIVSYSTEM FÜR SILICONE</p> <p>(57) Abstract</p> <p>The invention relates to a kit comprising the following: a) at least one resolubilizable (co)polymer, b) at least one adhesive for silicones, optionally c) a base body and optionally, d) a silicone compound. The invention also relates to the use of this kit for producing an impression tray.</p> <p>(57) Zusammenfassung</p> <p>Die vorliegende Erfindung betrifft ein Besteck, umfassend: a) zumindest ein wiederanlösbares (Co-)Polymer, b) zumindest ein Adhesiv für Silicone, gegebenenfalls c) einen Grundkörper, und gegebenenfalls d) eine Siliconmasse und die Verwendung dieses Bestecks zur Herstellung eines Abformlöffels.</p>		

ADHESIVE SYSTEM FOR SILICONES

The present invention relates to a kit for use in dentistry. In particular, the invention relates to a kit for bonding silicone compositions to a base surface made from polymers, polymers of methacrylates or fillers with the surface being part of a structure which includes an impression tray, dental crown, bridge, temporary crown or temporary bridge, comprising: a) at least one partially re-soluble (co-)polymer adapted to form a first layer on the base surface; and b) at least one adhesive for silicone adapted to form a second layer in an overlying relationship to the first layer, wherein the adhesive for silicones is a (co-)polymer or a mixture of (co-)polymers containing one or more groups selected from SiH, vinyl groups and silanol groups.

Impressions using impression compositions especially in the field of dentistry often require the use of so-called individually formed impression trays. Individual impression trays are individually manufactured mouldings in the form of an impression tray, which are manufactured, for example, from self-curing mixtures of methyl methacrylate/-polymethyl methacrylate or from photo-curable composite plates (consisting of multifunctional photo-curable (meth-)acrylate mixtures to which glass powder has been added), in dental applications called "photo-curable individual impression tray plates".

Silicones are usually used as impression compositions in the field of dentistry. The bond between the impression trays and silicones poses a problem, however; silicones do not by themselves adhere to plastics or composites. Nonetheless, in order to provide adhesion between silicone impression compositions and impression trays, attempts were firstly

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made to anchor the impression compositions stably in the impression tray, and to prevent them from lifting out of the impression tray after the impression has been taken, with the aid of mechanical retaining means, such as holes, undercuts, bent-round rims, etc., that is to say by purely mechanical means.

In a similar manner attempts were made in DE 42 28 538 to improve adhesion between the multiple use impression trays and a silicone impression composition by applying a dispersion on the metallic impression tray and drying the dispersion. Such systems also do not provide for sufficient adhesion of the silicone compositions on the impression trays.

Attempts were also made to improve the adhesion of the silicone compositions to impression trays by molecular/mechanical means with the aid of solutions of viscous silicone polymers. Generally such silicone impression tray adhesives are solutions of only partially crosslinked silicones in volatile solvents. Since no direct chemical bonding occurs between the silicone impression composition and the partially crosslinked silicone polymers of the impression tray adhesive, those adhesives can be used both for silicone impression compositions that are crosslinked by condensation and for those crosslinked by addition.

Both above-mentioned measures for better adhesion of the silicone impression compositions to the impression trays, however, provide unsatisfactory solutions: it is especially difficult to introduce mechanical retaining means into individually manufactured impression trays since they must be produced, for example, subsequently by boring. In the case of such rigid trays, boring also easily results in stress cracks; in addition, too many mechanical retaining holes weaken the impression trays' breaking strength and resistance to bending.

The commercially available solvent-containing viscous adhesives have only an auxiliary adhesive action: in the case of relatively strong tensile forces on removal of the impression from the object of which the impression is to be taken, such as a tooth, the silicone impression lifts up from the impression tray and becomes deformed and the viscous adhesive comes away with many drawn-out threads being formed. The deformation of the impression easily results in defective fittings.

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It has been known for a short time that adhesives that are used to bind non-hardening silicone re-lining materials securely to plastics for prostheses (e.g. accompanying Patent Application DE 199 05 224.7, Patent Application DE 196 35 696 A1 or Patent Specification EP 0 632 063 A1) also adhere excellently to impression trays that are slightly partially soluble. Partially soluble trays are, for example, trays made of polystyrene, polycarbonate. On monomer/polymer-based individual impression trays, such as, for example, those made of methyl methacrylate/polymethyl methacrylate, such adhesives can result in good adhesion of the silicone impression composition to precisely that type of individual impression trays.

It is problematic, however, to produce good adhesion of silicones to the surface of cross-linked methacrylates, especially to individual photo-curable impression trays based on a methacrylate composite, which are used in large numbers. The mentioned new adhesion primers for silicones fail on those types of polymerised kits.

The problem underlying the invention was therefore to provide a kit of parts that enables a reliable easy-to-produce bond between impression trays, such as impression trays consisting of methacrylate composites and especially special photo-curable individual impression trays, and silicone compositions, the bond being approximately as strong as the cohesion of the silicone composition itself.

According to the invention the problem is solved by a kit for bonding silicone compositions to a base surface made from polymers, polymers of methacrylates or fillers with the surface being part of a structure which includes an impression tray, dental crown, bridge, temporary crown or

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temporary bridge, comprising: a) at least one partially re-soluble (co-)polymer adapted to form a first layer on the base surface; and b) at least one adhesive for silicone adapted to form a second layer in an overlying relationship to the first layer, wherein the adhesive for silicones is a (co-)polymer or a mixture of (co-)polymers containing one or more groups selected from SiH, vinyl groups and silanol groups.

The kit will also optionally comprise a base body and/or a silicone composition.

Such trays are advantageous in that a chemical bond between the adhesive and the silicone composition takes place. Thereby the adhesion of the silicone composition - via the adhesive and the resolvable (co-)polymer - on the base body can be extremely tight. Such a tight adhesion cannot be achieved with known systems, especially not with systems, based on mechanical retention.

According to the invention, the base body may comprise or consist of polymers or copolymers of methacrylates. It may be a composite body and may additionally comprise fillers, such as glass powder.

The optionally comprised base body may be an impression tray, especially an individually manufactured impression tray and more especially an individually manufactured photo-curing impression tray. The base body may also be a dental crown or bridge or a temporary crown or bridge or bite plate made of composite material.

The soluble or partially (re-)soluble (co-)polymers may be or comprise, for example, polystyrene, polycarbonate, poly(meth-)acrylate, polyvinyl chloride, polysulphone, polymethylpentene or polystyrene acrylonitrile or mixtures thereof, the poly(meth-)acrylates preferably being polymers or mixed polymerisates of methyl, ethyl, propyl, butyl, neopentyl or tetrahydrofurfuryl esters of acrylic acids or methacrylic acids, on account of their being chemically related to the crosslinked methacrylates.

In principle, however, any soluble or partially (re-)soluble polymer is suitable that can bond with sufficient strength to (co-)polymerised base bodies, especially based on dimethacrylates or other multifunctional methacrylates to which fillers have been added or containing no fillers. A bond is sufficiently strong when it has an adhesive strength of at least 50%, more especially of at least 90% and most especially of at least 100% of the cohesive strength of the impression composition used.

According to the invention, preferably adhesives for silicone compositions are used, which react chemically with the silicone composition, i.e., which can build chemical bonds with the silicone composition.

The adhesive for silicones may be a (co-)polymer or a mixture of (co-)polymers containing SiH or vinyl groups; it is especially preferred for the (co-)polymer or the mixture of (co-)polymers to contain at least one SiH or vinyl group per unit, each unit corresponding to two originally used monomers.

Such adhesives are disclosed in the accompanying specification DE 199 05 224.7, to which reference is expressly made in respect of this disclosure.

Alternatively, the adhesive for silicones may be a (co-)polymer or a mixture of (co-)polymers containing silanol groups $-\text{Si}(X)-$ wherein X = OH, $-\text{O}-\text{R}_c$ or radicals of

the formulae $-\text{O}-\text{CO}-\text{R}_c$, $-\text{NR}_d-\text{R}_c$, $-\text{NR}_d-\text{CO}-\text{R}_c$, and the moieties R_c and R_d or the free bonds at the Si atom each independently of the others may be H atoms, OH groups, alkyl groups, alkoxy groups or aryl groups. It is especially preferred for the radicals of formulae $-\text{O}-\text{R}_c$, $-\text{O}-\text{CO}-\text{R}_c$, $-\text{NR}_d-\text{R}_c$, $-\text{NR}_d-\text{CO}-\text{R}_c$ to be readily hydrolysable radicals. Such groups of formula X are also disclosed in the accompanying PCT Patent Application "Adhesion promoters for silicone materials", Attorney Ref. No. 10730 filed at the European Patent Office on April 6, 2000 and the enclosed German Patent Application DE 199 15 492.9 to which reference is also expressly made in respect of this disclosure.

According to a preferred embodiment, the partially resolvable (co-)polymers and/or the adhesives for silicones are dissolved or partially dissolved in at least one readily volatile inert solvent. An aliphatic or aromatic, halogenated or non-halogenated hydrocarbon, ether, ketone, ester or cyclic siloxane may be used as solvent. Such solvents are per se known to a person skilled in the art.

applied to the surface of the individual impression tray. This is effected easily by applying the polymer dissolved in readily volatile inert solvents.

As described above, base bodies, such as methacrylate base bodies, that have been treated with soluble polymers are treated according to the invention in a second step with silicone adhesion promoters (primers), as described, for example, in the accompanying Patent Application DE 199 05 224.7 or in Patent Application DE 196 35 696 A1 or in Patent Specification EP 0 632 060 A1 for addition-crosslinking systems (A), or as also described, for example, in the accompanying PCT Patent Application "Adhesion promoters for silicone materials", Attorney Ref. No. 10730 filed at the European Patent Office on April 6, 2000 and the enclosed German Patent Application DE 199 15 492.9, for condensation crosslinking systems (K).

Suitable primers (A) for coating base bodies, especially individual photo-cured impression trays, with addition-crosslinking impression compositions may be solutions of adhesive polymers that comprise a sufficient amount of SiH or vinyl groups and that can dissolve adequately in the applied polymer surface of the dimethacrylate base body, sufficiently volatile solvents being used. Especially the above described solvents can be used. Impression trays treated in that manner are ready and suitable for strong adhesion of addition-crosslinking silicones.

Suitable primers (K) for coating impression trays with condensation-crosslinking impression compositions may be, for example, solutions of polymers comprising a sufficient amount of silanol groups $-\text{Si}(\text{X})-$, wherein $\text{X} = \text{OH}, -\text{O}-\text{R}_2,$

$-O-CO-R_c$, $-NR_d-R_c$, $-NR_d-CO-R_c$, and the moieties R_c and R_d are as defined above, the solutions of the polymers being able to dissolve adequately in the applied polymer surface (1st layer) of the dimethacrylate impression tray and the solvents used being sufficiently volatile. Especially the above described solvents can be used. Impression trays treated in that manner are ready and suitable for strong adhesion of condensation-crosslinking silicones to that surface.

The kit of parts and impression tray according to the invention can be used for medical applications, especially for dental applications, their use as impression trays for silicone compositions being especially preferred. The impression compositions used are, for example, silicone compositions for taking impressions of teeth.

In the case of individual impression trays, the trays prepared in that manner can be charged directly with impression composition of the appropriate curing type at the dentist's and inserted into the mouth in order for the impression to be taken. On removal of the charged impression tray, the impression composition and the impression tray remain securely bonded. Portions of the cured impression composition do not become detached from the impression tray, and corresponding distortions and defective impressions do not occur. Attempts to remove the impression composition from the impression tray result in impression material breaking away.

Many other applications of bonding silicones to crosslinked methacrylate plastics are conceivable and in line with the invention.

For example, with the aid of the adhesive system according to the invention flexible silicone gum masks can be secured at the lower edge of composite-lined dimethacrylate-based dental crowns or bridges or temporary crowns or bridges in order to cover up insufficient gingival margins.

For example, with the aid of the adhesive system according to the invention the inside of composite bite plate can be treated and lined with curing elastic silicone.

Moreover, where patients have contact allergies to contents of composites, the composites can be coated according to the procedure of the patent with a thin layer of curing silicone, or composite mouldings in industrial applications can be coated in a manner according to the patent and flexibly bonded lastingly with a silicone adhesive.

EXAMPLES

Adhesion of an addition-crosslinking silicone impression composition to a photo-curable individual impression tray.

A photo-curable impression tray plate (Megatray, made by Megadenta, Germany) is shaped on a plaster model to form an impression tray and is photo-cured for 3 minutes in an irradiation unit (Megaflash, made by Megadenta). The oxygen-inhibiting layer on the surface is removed from the inner face of the resulting impression tray by means of an alcohol-impregnated cloth.

A 15% solution of a soluble polymer powder (polymethyl methacrylate MW332, made by Röhm, Germany) in toluene is prepared and this is applied thinly to the cleaned inner face of the impression tray and is left to dry.

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The silicone adhesion primer corresponding to Example 2 of the accompanying Patent Application DE 199 05 224.7 is then applied to the so treated inner face and is dried. The impression tray is then loaded with the addition-crosslinking silicone pre-impression composition R-si-line putty (R-Dental, Germany) and an impression is taken in the mouth of the teeth of an upper jaw. After curing, the impression tray with the cured impression composition is removed without a trace of the silicone becoming detached from the inner face of the impression tray. The impression composition is bonded securely to the impression tray and can be removed only by destroying the impression composition.

CLAIMS:

1. A kit for bonding silicone compositions to a base surface made from polymers, polymers of methacrylates or fillers with said surface being part of a structure which includes an impression tray, dental crown, bridge, temporary crown or temporary bridge, comprising:
 - a) at least one partially re-soluble (co-)polymer adapted to form a first layer on said base surface; and
 - b) at least one adhesive for silicone adapted to form a second layer in an overlying relationship to said first layer, wherein the adhesive for silicones is a (co-)polymer or a mixture of (co-)polymers containing one or more groups selected from SiH, vinyl groups and silanol groups.
2. The kit according to claim 1 further comprising:
 - c) a base body.
3. The kit according to claim 2 further comprising:
 - d) a silicone composition.
4. The kit according to claim 2 wherein the base body comprises polymers or copolymers of methacrylates.
5. The kit according to claim 2 wherein the base body additionally comprises one or more fillers.
6. The kit of Claim 5 wherein the filler is a glass powder.

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7. The kit according to claim 2 wherein the base body is an impression tray, a dental crown, bridge, temporary crown, or a temporary bridge.
8. The kit according to claim 1 wherein the partially resoluble (co-)polymers comprise polystyrene, polycarbonate, poly(meth-)acrylate, polyvinyl chloride, polysulphone, polymethylpentene, polystyrene acrylonitrile or mixtures thereof.
9. The kit according to claim 8 wherein the poly(meth-)acrylates comprise polymers or mixed polymerisates of methyl, ethyl, propyl, butyl, neopentyl or tetrahydrofurfuryl esters of acrylic acids or methacrylic acids.
10. The kit according to claim 1 wherein the partially resolvable (co-) polymers and/or the adhesives for silicones are dissolved or partially dissolved in at least one readily volatile inert solvent.
11. The kit according to claim 10 wherein the solvent is an aliphatic or aromatic, halogenated or non-halogenated hydrocarbon, ether, ketone, ester, or cyclic siloxane.
12. The kit according to claim 3 wherein the silicone composition comprises a silicone impression composition for taking impressions of teeth.
13. The kit according to claim 1 wherein components a) and b) are present in separate containers.
14. The kit according to claim 2 wherein components a), b), and c) are present in separate containers.

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15. The kit according to claim 3 wherein components a), b), c), and d) are present in separate containers.

16. A method of manufacturing a molding, comprising the steps of:

- a) applying a solution of at least one partially resoluble (co-)polymer to at least one surface of a composite;
- b) drying the partially resoluble (co-)polymer(s);
- c) applying a solution of at least one adhesive for silicones to the layer of the partially resoluble (co-)polymer(s); and
- d) drying the adhesive(s).

17. The method of manufacturing a molding according to claim 16 further comprising applying a silicone composition to the adhesive(s).

18. The method of manufacturing a molding according to claim 16 wherein the partially resoluble (co-)polymer and/or adhesive for silicones are dissolved in at least one solvent.

19. The method of manufacturing a molding according to claim 18 wherein the solvent is a readily volatile inert solvent.

20. The method of manufacturing a molding according to claim 19 wherein the partially resoluble (co-)polymers comprise polystyrene, polycarbonate, poly(meth-)acrylate, polyvinyl chloride, polysulphone, polymethylpentene, polystyrene acrylonitrile or mixtures thereof.

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21. The method of manufacturing a molding according to claim 20 wherein the poly(meth-)acrylates comprise polymers or mixed polymerisates of methyl, ethyl, propyl, butyl, neopentyl or tetrahydrofurfuryl esters of acrylic acids or methacrylic acids.

22. The method of manufacturing a molding according to claim 16 wherein the adhesive for silicones is a (co-)polymer or a mixture of (co-)polymers which comprise one or more groups selected from SiH, vinyl groups and silanol groups.

23. The kit according to claim 1, wherein the base surface is used for manufacturing a molding or an impression tray for silicone compositions.