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(54) Titre : PREPARATION ADHESIVE POUR PROTHESES DENTAIRES
(54) Title: ADHESIVE PREPARATION FOR DENTAL PROSTHESES

(57) Abrégé/Abstract:
The invention relates to a vegetable-based adhesive preparation for dental prostheses, said preparation having improved adhesive properties, consistency and stability as a result of a filler containitw: 35 to 45 wt % vegetable oil; 25 to 50 wt % structure-forming stabilizer; 5 to 15 wt % bonding agent; and silicon oxide making up the remainder.

ABSTRACT

The invention relates to a vegetable-based adhesive preparation for dental prostheses, said preparation having improved adhesive properties, consistency and stability as a result of a filler containing: 35 to 45 wt % vegetable oil; 25 to 50 wt % structure-forming stabilizer; 5 to 15 wt % bonding agent; and silicon oxide making up the remainder.

Adhesive Preparation for Dental Prostheses

The present invention pertains to an adhesive preparation for dental prostheses.

Such an adhesive preparation for dental prostheses is known from DE 10 2005 031 771. The adhesive preparation there contains viscous paraffin in a percentage of 25 wt.% to 35 wt.% and/or white vaseline in a percentage of 10 wt.% to 20 wt.% as the cream basis, a carbomer (polyacrylic acid) as a bonding agent with a percentage of 1 wt.% to 15 wt.% as well as one or at least two carboxymethylcellulose(s) or an alkali metal salt or alkaline earth metal salt of same as a bonding agent with a percentage of 15 wt.% to 50 wt.% as well as highly disperse silicic acid as a filler with 0.2 wt.% to 2.0 wt.%.

Commercially available adhesive creams use paraffin/vaseline to obtain a pliable preparation. In prosthesis wearers, irritations of parts of the pharynx may occur. The commercially available adhesive creams for prostheses also use for the most part the raw material GANTREZ® (calcium/sodium PVM/MA copolymer) from the firm of ISP, with regard to which is given the risk of possible raw material shortages, raw material dependencies and time delays of the raw material availability.

Therefore, it was already suggested in practice to use olive oil instead of paraffin or Vaseline® as the carrier substance. The prior-art adhesive cream has, however, only an adhesiveness in the lower acceptable range at best.

If one wants to replace paraffin or Vaseline® with a vegetable oil, then the remaining components of the starting adhesive preparation may not be retained as such. Because of the completely different consistency of olive oil compared to Vaseline® or paraffin, no acceptable adhesive preparation is then obtained.

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In this case, the requirements on such an adhesive cream with regard to adhesiveness, consistency and stability must be taken into account.

Hence, the basic object of the present invention is to create an adhesive preparation for dental prostheses, which is nevertheless suitable as such while dispensing with paraffin and/or Vaseline® as the basic or cream substance and has especially not only good subjective, but also objective adhesive properties as well as, in addition, a homogeneous consistency and high stability over time.

According to the present invention the object mentioned is accomplished by an adhesive preparation for dental prostheses containing

- 35 wt.% to 50 wt.% vegetable oil,
- 25 wt.% to 50 wt.% structure-forming stabilizer,
- 5 wt.% to 15 wt.% bonding agent, and
- the remainder being a filler containing silicon oxide.

Preferably, the adhesive cream consists exclusively of these components. The sum of vegetable oil and stabilizer lie below 90 wt.% here.

The filler or its at least decisive main component silicon dioxide (silica) is highly porous, i.e., the filler and/or silicon dioxide has a density of 1.9 g/cm^3 to 2.1 g/cm^3. While silicon dioxide is usually prepared as fused or pyrogenic silicon dioxide, provisions are made in a preferred embodiment for the filler to contain silicon dioxide precipitated from a solution. According to another preferred embodiment, provisions are made for the particle size to lie in the range of 1 μm to 40 μm. Particle size here does not designate the primary particle size, which lies at 5-100 nm, but the size of the particles formed by agglomeration of the primary particles, or of the agglomerate particles or the size of the agglomerate. The average pore size is preferably > 30 nm. While the surface of the particles preferably is in the range of 5 m^2/g to 100 m^2/g, this value is most preferably < than 50 m^2/g.

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As the replacement for paraffin VASELINE®, vegetable oils guarantee the pliability of the preparation. With the use of vegetable oils, based on the chemical composition, an anti-inflammatory effect can be achieved in the event of corresponding irritations. The bonding agent contributes to the pliability as well. The filler brings about the necessary thickening and regulates the viscosity.

It was determined that besides olive oil, especially also Saint John's wort oil, almond oil, rapeseed oil, soybean oil, sunflower seed oil, grapeseed oil and/or wheat germ oil are also preferably possible as vegetable oil.

Carboxymethylcellulose (CMC), especially as sodium salt, but also as other alkali salt or alkaline earth salt of the said cellulose or hydroxyethylcellulose (HEC), especially Walocel™, is preferably provided as a structure-forming stabilizer with the percentage mentioned. As an alternative, the adhesive preparation according to the present invention may also contain hydroxypropylcellulose (HPC) or xanthan gum as a structure-forming stabilizer.

The bonding agent in the adhesive preparation according to the present invention preferably contains polyacrylic acid with the above-mentioned weight percentage, whereby the bonding agent is preferably polyacrylic acid, and is especially the exclusive bonding agent. Thereby, the bonding agent with a dynamic viscosity equal to or greater than 30,000 mPas is preferably used. Carbomers especially represented by the trade names Carbopol® 971P NF and Carbopol® 974P NF are possible as concrete polyacrylic acid or carbomers. By means of this bonding agent, the bonding agent usually used in an adhesive composition (methyl vinyl ether), maleic acid anhydride (copolymer), which contains zinc, which is considered to be harmful, can be avoided.

Preferred embodiments of the present invention provide for the filler to be highly porous, for the filler to contain silicon dioxide precipitated from a solution, for the density of the filler, preferably at least of the silicon dioxide essentially constituting it, to be between 0.08 g/cm^3 and 0.23 g/cm^3, preferably between 0.19 g/cm^3 and 0.21 g/cm^3, and/or for the particle size to lie in the range of 1 μm to 40 μm, whereby the average pore size is preferably > 30 nm.

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While the filler may consist exclusively of silicon oxide (silica), in the preferred embodiment, it contains a low percentage of less than 0.1 wt.%, but preferably at least 0.001 wt.%, most preferably at least 0.01 wt.% styrene-isoprene copolymer and/or less than 0.1 wt.%, preferably at least 0.001 wt.%, most preferably at least 0.01 wt.% aluminum stearate.

While the compositions mentioned above guarantee suitable adhesive preparations for dental prostheses with the weight percentages given there, provisions are made in a preferred embodiment for 40 wt.% to 50 wt.% to make up the vegetable oil percentage, 40 wt.% to 50 wt.% to make up that of the structure-forming stabilizer, 8 wt.% to 13 wt.% to make up the bonding agent and/or 3 wt.% to 6 wt.% to make up the filler, whereby the sum of all components amounts to 100 wt.% in each case..

An adhesive preparation with a plastic, soft consistency, which is neither too stiff nor too flowable, is created by the present invention. The adhesive preparation has, moreover, a suitable adhesive force above a lower acceptable value of 40 N, without the risk of a too high adhesive force of over 150 N, especially over 180 N being given.

Moreover, the adhesive preparation according to the present invention has a high stability over time and does not decompose even in the event of a long storage time.

Further advantages and features of the present invention appear from the claims and from the following description, in which exemplary embodiments of the adhesive preparation according to the present invention are explained. Here,

Figure 1 shows adhesive force values for various adhesive preparations.

Figure 1 shows adhesive force mean values from two measurements in Newtons (N) for a plurality of commercially available adhesive preparations, which are designated with A through P as well as two adhesive preparations according to the present invention based on olive oil, on the one

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hand, and based on soybean oil, on the other hand, whose exact composition appears from Tables 1 through 3.

The adhesive composition H is the composition known from practice, which is based on olive oil and does not contain earth-oil-based basic substances, such as paraffin or Vaseline®, which are given I through P with all other adhesive compositions A through G.

It is shown that while the prior-art, olive-oil-based adhesive composition has a comparably extremely low adhesive force of less than 20 N with otherwise acceptable adhesive values of over 40 N or 50 N, while the likewise vegetable-oil-based adhesive force compositions according to the present invention V-E-11-hcolive 11 and VE-E-11-hcsoja11 show optimal adhesive force values in the range of over 90 N, whereby, as stated, adhesive force values of over 50 N are still completely acceptable, which, however, are obtained up to now only by paraffin-based or vaseline-based adhesive compositions.

The filler of the tables is continuously silicon-oxide-based filler with 99% silicon oxide (silica) and low percentages of styrene-isoprene copolymer and aluminum stearate of less than 0.1 wt.% each. If no specific data are contained in each of the tables, the component designations and percentages indicated in the heading of the tables apply. Deviating components are themselves optionally indicated in the individual fields of the table, just as deviating percentages of the components indicated in the heading.

The adhesive force and consistency measurements, which are the basis of the Tables 1 through 3 attached as appendices, are carried out as follows, the latter analogous to DIN 10331/ISO 16305:

The adhesive force measurements are carried out with the structure measuring apparatus A-XT plus from Stable Micro Systems Ltd., Godalming, Surrey, Great Britain. For the measurement, 0.75 g (± 0.01 g) of adhesive cream with a sample temperature of 25°C ± 1°C was applied to an unengraved

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side of the sample holder in lumps. The forward and testing speeds are each 0.5 mm/sec, the return speed is 10.0 mm/sec. The pressing pressure was 1,000.0 g, and the trigger value was 5.0 g. Five hundred measurement points were determined per measurement.

The consistency measurement was carried out such that 1.0 g of the test substance tempered to 20°C is applied in lumps to a glass plate in the middle. The glass plate with the test substance was placed on the extensometer, tempered to 20°C, for 10 min. to 15 min., before another glass plate (diameter = 11.5 cm) with a weight of 47.85 g was placed on. Then, the upper glass plate was weighted down with the test weight of the apparatus of 331.3 g (total weight 379.15 g). The diameter of the circle or ellipse formed was determined after 15 min.

An extremely preferred formulation V-E-11-hcsoja-11 according to the present invention containing 42 wt.% soybean oil, 9 wt.% polyacrylic acid as bonding agent, as is represented by the designation Carbopol 971P NF from the Lubrizol Corporation, Wickliffe, Ohio, USA, 44 wt.% of carboxymethylcellulose sold, for example, by the Dow Deutschland Anlagengesellschaft mbH, Schwalbach under the designation WALOCEL™ as structure-forming stabilizer and 5 wt.% filler is shown in line 1 in Table 1. This adhesive preparation has an optimal – soft – consistency of 4.4 cm to 4.5 cm with an adhesive force of 92 N, as Figure 1 shows.

While the formulations 4 through 6 of Table 1 with consistencies between 3.5 cm and 3.8 cm have a likewise acceptable adhesive force of 63 N to 76 N, it is shown that the consistency of the adhesive preparation is too stiff or too firm (formulation 2 of Table 1) in the event of a sharper reduction of the vegetable oil percentage with simultaneous increasing of the carboxymethylcellulose percentage to markedly above 50%, and this may also not be compensated by reducing the filler (formulation 3 of Table 1).

Table 2 shows that the structure-forming stabilizer carboxymethylcellulose (Walocel) may basically also be completely – or even partially – substituted by the structure-forming stabilizer xanthan gum, whereby the adhesive force decreases slightly compared to carboxymethylcellulose, but absolutely also lies markedly above the lower limit of 40 N. Therefore, the table shows also that bonding

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agents with a markedly higher viscosity than 29,000 mPa may be used and absolutely very good adhesive values with suitable consistency are obtained.

Adhesive preparations according to the present invention have a body-compatible, particularly also mucous-membrane-compatible slightly acidic pH value of more than 5.

Surprisingly, formulations 4 and 5 of Table 3 show that the use of a suitable bonding agent – as used in the other compositions – a means suitable as a structure-forming stabilizer, such as Keldent™, leads to a dramatic drop in the adhesive force, aside from the fact that the adhesive preparation is, moreover, also too stiff.

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Appendix 1

Table 1

ADHESIVE CREAM TEST SERIES 2011

		Natural oil		Carbopol 971P NF		CMC		Filler		PHYSICAL PROPERTIES
		30%	45%	5%	15%	30%	50%	3%	6%	
1	FORMULATION V-E-11-hcsoja-11		42%	9%			44%		5%	Consistency = 4.4/4.5 cm Adhesive force = 92 N
2	V-E-11-hcsoja-12-a	x		9%			56%		5%	=> too firm, pliability absent!
3	V-E-11-hcsoja-12	x		9%			58%	x		=> too firm, pliability absent!
4	V-E-11-hcsoja-13		x	9%			40%		x	Consistency = 3.8/3.8 cm Adhesive force = 76 N
5	V-E-11-hcsoja-14		x	x			44%		x	Consistency = 3.5/3.6 cm Adhesive force = 63 N
6	V-E-11-hcsoja-15		x		x	34%			x	Consistency = 3.5/3.5 cm Adhesive force = 75 N

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Appendix 2

Table 2

ADHESIVE CREAM TEST SERIES 2011

		Natural oil		Carbopol 974P NF		Structure		Filler		PHYSICAL PROPERTIES
		30%	45%	5%	15%	25%	45%	3%	6%	
1	FORMULATION V-E-11-hcsoja-11		42%	9% Carbopol 971P NF			44% Walocel™ 60,000		5%	Consistency = 4.4/4.5 cm Adhesive force = 92 N
2	V-E-11-hccarb974-2		45%	15%			35% Walocel™ 60,000		5%	Consistency = 3.6/3.6 cm Adhesive force = 78 N
3	V-E-11-hccarb974-3		45%	12%			38% Keldent™		5%	Consistency = cm Adhesive force = 77 N
4	V-E-11-hccarb974-4		42%	9%			44% Keldent™		5%	Consistency = 3.6/3.6 cm Adhesive force = 69 N

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Appendix 3

Table 3

ADHESIVE CREAM TEST SERIES 2011

		Natural oil*		Carbopol 971P NF**		CMC (or) HEC (or) Xanthan Gum***		99% Silica**** < 0.1% styrene/isoprene copolymer < 0.1% aluminum stearates		PHYSICAL PROPERTIES
		30%	45%	5%	15%	25%	45%	3%	6%	
1	FORMULATION V-E-11-hcsoja-11		42%	9%			44% Walocel™ 60,000		5%	Consistency = 4.4/4.5 cm Adhesive force = 92 N
2	V-E-11-hckel-1		42%	9%			44% Keldent™		5%	Consistency = 4.0/4.0 cm Adhesive force = 72 N
3	V-E-11-hckel-2		42%	9%			44% Keltrol CG		5%	Consistency = 2.9/3.0 cm Adhesive force = 25 N
4	V-E-11-hckel-3		42%	--			53% Keldent™		5%	Adhesive force = 1.3 N => too firm, pliability absent!
5	V-E-11-hckel-4		42%	9% Keldent™			44% Walocel™ 60,000		5%	Adhesive force = 0.6 N => too firm, pliability absent!

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6	V-E-11-hcnat-1		42%	9%			44% Natrosol™ HX		5%	Adhesive force = 39 N => too firm, gritty, pliability absent!

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CLAIMS:

1. Adhesive preparation for dental prosthesis comprising
- 35 to 50 wt.% vegetable oil,
- 25 to 50 wt.% structure-forming stabilizer carboxymethylcellulose (CMC) or xanthan gum,
- 5 to 15 wt.% of adhesive,
- 3 to 6 wt.% silica-containing filler,

the sum of all constituents being 100 wt.%,
wherein the adhesive contains polyacrylic acid, and the filler comprises solution precipitated silica having a density between 0.08 and 0.23 g/cm^3 and is highly porous.

2. Adhesive preparation according to claim 1, wherein the vegetable oil is St. John's wort oil, almond oil, olive oil, rapeseed oil, soybean oil, sunflower oil, grape seed oil, and/or wheat germ oil.

3. The adhesive preparation according to claim 1 or 2, wherein the density of the filler is between 0.19 and 21 g/cm^3.

4. Adhesive preparation according to claim 3, wherein the density of at least the silica substantially constituting the filler is between 0.19 g/cm^3 and 0.21 g/cm^3.

5. Adhesive preparation according to any one of claims 1 to 4, wherein a particle size of the filler is in a range of 1 to 40 microns.

6. Adhesive preparation according to claim 5, wherein the average pore size of the filler is greater than 30nm.

7. Adhesive preparation according to any one of claims 1 to 6, wherein the filler contains less than 0.1 wt.% of styrene-isoprene copolymer based on filler weight.

8. Adhesive preparation according to any one of claims 1 to 7, wherein the filler contains at least 0.001 wt.% of styrene-isoprene copolymer based on filler weight.

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9. Adhesive preparation according to claim 8, wherein the filler contains at least 0.01 wt.% of styrene-isoprene copolymer based on filler weight.

10. Adhesive preparation according to any one of claims 1 to 9, wherein the filler contains less than 0.1 wt.% of aluminum stearate based on filler weight.

11. Adhesive preparation according to any one of claims 1 to 10, wherein the filler contains at least 0.001 wt.% of aluminum stearate based on filler weight.

12. Adhesive preparation according to claim 11, wherein the filler contains at least 0.01 wt.% of aluminum stearate based on filler weight.

13. Adhesive preparation according to any one of claims 1 to 12, wherein the adhesive force of the adhesive preparation is between 40 and 150N.

14. Adhesive preparation according to claim 13, wherein the adhesive force of the adhesive preparation is between 70 and 110N.

15. Adhesive preparation according to any one of claims 1 to 14, comprising the vegetable oil at a content of 40 to 45 wt.%.

16. Adhesive preparation according to any one of claims 1 to 15, comprising the structure-forming stabilizer at a content of 40 to 50 wt.%.

17. Adhesive preparation according to any one of claims 1 to 16, comprising less than 10 wt.% of the adhesive.

18. Adhesive preparation according to claim 17, comprising at most 9 wt.% of the adhesive.

19. Adhesive preparation according to any one of claims 1 to 17, wherein the preparation comprises 40 to 45 wt.% vegetable oil, 41 to 46 wt.% structure-forming stabilizer, 7 to less than 10 wt.% of the adhesive and 4 to 6 wt.% of the silica-containing filler.

20. Adhesive preparation according to claim 19, comprising at most 9 wt.% of the adhesive.

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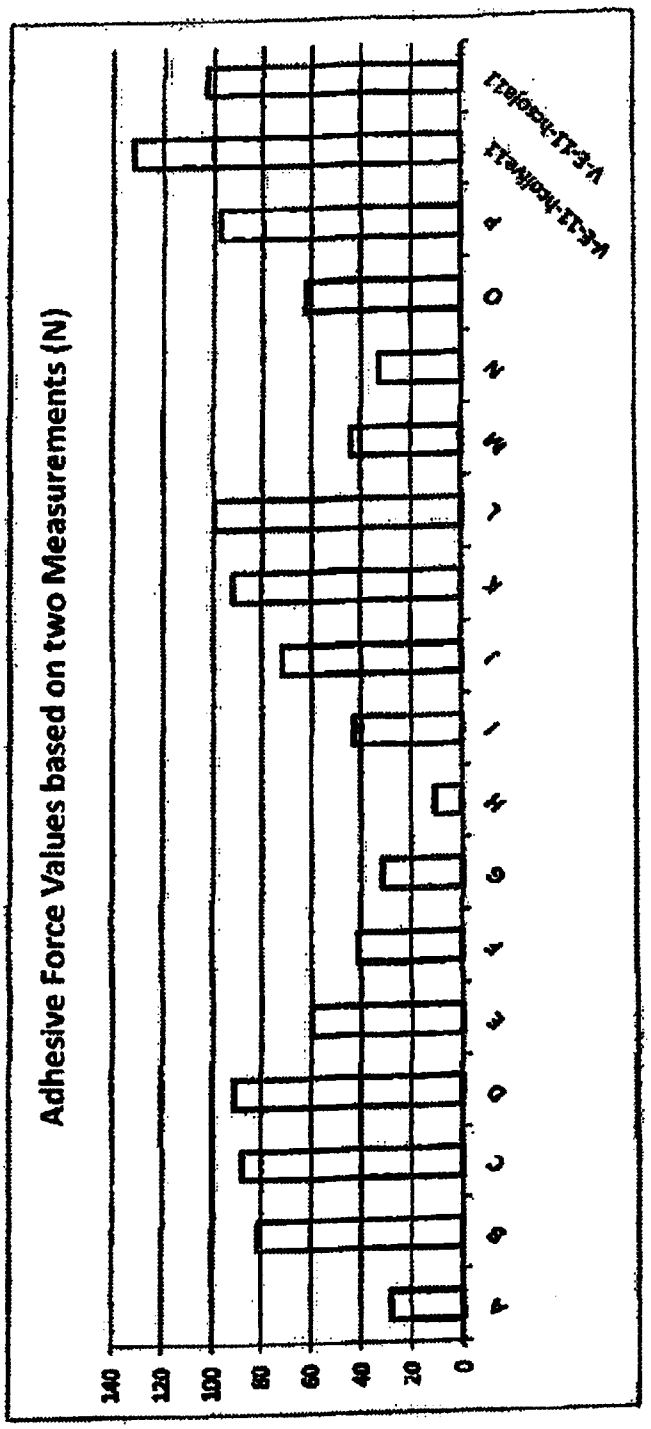
Adhesive Force Values based on two Measurements (N)
140
120
100
80
60
40
20
0

Fig.1