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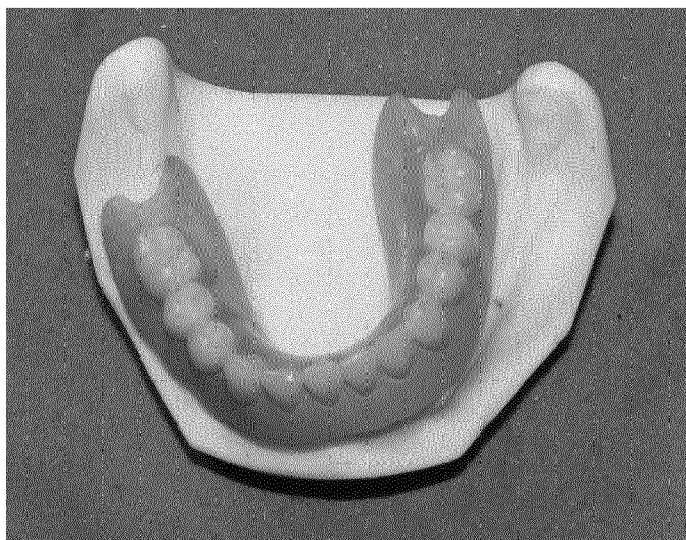


Fig. 3

(57) Abstract: Dental prostheses obtainable starting from a model prosthesis, obtainable by polymer moulding starting from a dental plaster cast, and subjecting the model prosthesis to a thermal treatment at temperatures in the range 105°C-250°C under atmospheric pressure, the model prosthesis complying with the following test: a strip of the model prosthesis polymer, having 6X6X80 mm sizes, takes the external form of a metal cylinder having a diameter of 30 mm, a concavity with curvature radius 12 mm and curvature centre in the Cartesian coordinate system 15 mm and 15 mm, a convexity with curvature radius 8 mm and curvature centre in the Cartesian coordinate system 8 mm and 8 mm; the strip, after being subjected to thermal treatment, is let adhere to the cylinder by applying a force up to 1 kg weight and it reproduces the external surface thereof without showing any fracture or cracks.

DENTAL PROSTHESES

The present invention relates to dental prostheses and the process for the preparation thereof.

More specifically the invention relates to dental prostheses obtained starting from a predefined prosthesis suitable for the preparation of any type of dental prosthesis.

It is well known that for the preparation of dental prostheses several steps and long and complex procedures are requested. The conventional technique used to obtain dental prostheses requires several time consuming steps and relevant costs both for the patient, the dentist and the dental practitioner. For example in a first appointment of the patient with the dentist, impressions of the dental arches are taken by using a composition formed of alginate and/or an elastomer by means of a metal impression tray. Then the colour of the teeth to be inserted in the prosthesis is selected as more as possible identical to that of the patient's teeth. The obtained impressions are then sent to the dental practitioner wherein plaster casts of the upper and lower arch are prepared therefrom. Once the plaster cast is hardened, the models are mounted on an articulator. At this point a wax prosthesis is prepared with inserted the teeth having prescribed shape and colours. The wax prosthesis is melted, for example in a muffle, while injecting the prosthesis polymer, obtaining the raw prosthesis. The dental practitioner refines, finishes and polishes the dental prosthesis that is then tested in the articulator, in order to regulate bite. The so obtained dental prosthesis is modified as requested by the dentist, for instance by using small bench cutters, to better adapt the dental prosthesis to the patient mouth. When the modifications are more substantial, generally it is preferred to repeat the process and prepare a new prosthesis. To conclude, the conventional technique requires rather long times. Furthermore each prosthesis must be prepared case by

case by the dental practitioner.

It is known in the art USP 5,304,063, which describes a denture adapted to be positioned on an edentulous gum and on the surfaces of the surrounding tissues thereto, and a method to produce and insert complete dentures which comprise a thermally deformable base. The denture support has an inner surface and an external surface and is obtained by a moulding process from a doughy mixture formed of a plasticized liquid monomer and by a methylmethacrylate polymer powder in a 1:3-3.5 ratio. When heated to a temperature higher than about 135°F (~57°C) the denture support becomes malleable and can be moulded in the patient mouth to make the denture support adhere to the gum surface. The denture support can then be assembled in a complete denture by crosslinking a liner of an unpolymerized resin on the inner surface of the support, inserting then teeth on its external surface. In particular the patent claims a method to produce and adapt a modular prosthesis to the patient mouth, comprising the following steps:

- preparation of the prosthesis support as defined above;
- heating the denture support at temperatures higher than 135° F (57°C) in order to make the support malleable;
- insertion of the prosthesis support in the patient mouth by applying pressure to adapt the support to the edentulous gum and to the surrounding tissues of the patient mouth;
- removal of the prosthesis support from the patient mouth;
- fitting of an unpolymerized resin liner on the inner surface of the prosthesis support;
- insertion of the prosthesis support in the patient mouth by applying pressure to create a final detailed impression of the edentulous gum and of the surrounding tissues of the patient mouth;
- removal of the denture support from the patient mouth;
- crosslinking of the resin liner;
- insertion of the teeth in the external surface of the denture support.

Heating at the temperature of 57°C can be obtained by

immersion in a warm water bath. The polymerization of the liner can be obtained by hardening through polymerization with various methods, comprising light, heat or chemical reagents. The bond between the liner and the crosslinked support of the prosthesis is such as to stabilize the support so that it is not deformed when the patient takes food or warm drinks. In the description it is stated that the teeth can be fixed to the support before or after the prosthesis support has been fitted into the patient mouth.

In this patent the preparation of a support fitting onto the edentulous gum and a liner to attach the prosthesis to the support, are required.

USP 5,775,900 describes a transparent stent for diagnostic or surgical applications, thermally deformable, that can be inserted on a fully or partially edentulous gum and the surrounding tissues, and a method to produce and fit the stents in the gums. The patent relates furthermore to a kit comprising a stent couple having the above defined characteristics, of which one being the impression of the other, and a temporary prosthesis, thermally deformable like the stent, and a method for its production. The stent and the prosthesis are prepared from a dough mixture having the same composition as that described in USP 5,304,063. When the mixture is heated at temperatures higher than 120°F (49°C) the stent and the prosthesis become malleable and can be shaped in the patient mouth or on a corresponding model, to adapt them to the surfaces of the tissues. More specifically the patent relates to the field of prosthodontic implants wherein teeth are re-inserted to their place through a fixed or removable implant. For preparing these implants a surgical and/or radiographic stent made of a transparent acrylic resin is used, that in the moulded form keeps a high accuracy degree. Furthermore by this kit the dental practitioner can prepare a surgical and/or radiographic stent and a fully aligned and functioning interim or temporary prosthesis, to take impressions to both dentulous and edentulous patients in order to prepare per-

manent prostheses. The purpose of this patent is to eliminate the various steps in the clinic and in the laboratory in the process of preparation of surgical/radiographic stents for implants and temporary prostheses. This is achieved by preparing various stents, wherein the base sizes are respectively small, medium or large, with various tooth arrangements on the base. The stent resin can be dipped in water at 120°-160° F (49°-71°C) to make it deformable. Once molded and cooled, the base remains stable. The tooth position and aesthetics can be checked and corrected if necessary. The transparent acrylic resin base can be coloured to make it similar to the gum tissue. The ad interim or temporary prostheses, as the stents, can be dipped in water at 49-71°C to make them shaped. The denture can then be molded to fit the correct anatomic configuration of the patient's mouth. Also teeth are made of acrylic material and mounted on the base. The kit described in the patent is used for diagnostic purposes, see in the block diagram of Fig. 4A of the patent, step 8 that refers to Fig. 4B. As said above also temporary prostheses can be prepared for diagnostic use in order to correctly position the teeth of the upper jaw in correspondence with those of the lower jaw and check whether they properly close, that is to control their height. A further diagnostic use is that as surgical guides to establish where to insert the implants in order to insert a new tooth when the natural tooth has been removed. A further diagnostic use is that for radiologic purposes wherein a marker is contained in the base of the stent to position the implants. To conclude, in this patent permanent prostheses suitable for eating food are not described but their application is limited to the preparation of surgical guides for the precise insertion of the implants. These kits for these applications are well known to the skilled in the field.

US patent application 2004/0248065 relates to embodiments comprising either a lower denture or an upper denture without a palate, or a set of dentures containing both the

lower and upper denture. The denture comprises a layer of a reline material. These embodiments are adapted to the mouth of the patient by dipping the denture in warm water to soften the reline material. Generally the temperature of warm water is higher than room temperature (18°-21°C, corresponding to 66-71°F) but lower than 100°C (212°F); or the water temperature can range from 45°C (112°F) to 80°C (176°F) or from 51°C (125°F) up to 58°C (135°F). The dipping time of the material in water, in order to soften the reline material, ranges from 2 to 10 minutes. Generally the water temperature can range from 38°C (100°F) to 95°C (204°F). The thickness of the reline material is in the range from about 1 to about 5 mm, preferably from 1.5 to 3 mm. When the reline material is softened, the prosthesis is adapted inside the mouth and a force is applied on the denture for some minutes. In this time interval the reline material conforms to the mouth and to the gum of the patient, thus avoiding both an appointment for taking impressions of the gum and surrounding tissues and returning to the dentist for prosthesis adjustments. This patent application relates to reline materials or products well known on the market, such as for example those sold under the trademark Hydrocast®. These reline materials are inserted in the inner part of the prosthesis to form an adhesive pad to fix the prosthesis. This patent application describes therefore a reline material to let adhere a prosthesis to the gum in order to fix the prosthesis.

The need was felt to have available dental prostheses adaptable to plaster casts of gums overcoming the prior art drawbacks, being obtainable by a simplified process, substantially reducing the number of reprocessing steps requested to adapt the prostheses to the various casts and allowing furthermore to avoid the formation of scraps when the dental prosthesis prepared by the dental practitioner is not suitable for dental use.

The Applicant has unexpectedly and surprisingly found the solution to the above mentioned technical problem as

specified hereinafter.

It is an object of the present invention dental prostheses obtainable starting from a model prosthesis, obtainable by polymer moulding starting from a plaster cast of a dental arch, and subjecting the model prosthesis to thermal treatment at temperatures in the range 105°C-250°C under atmospheric pressure, the model prosthesis satisfying the following test:

a strip having 6X6X80 mm sizes of the polymeric material that forms the model prosthesis takes the external form of a metal cylinder having a diameter of 30 mm and a concavity with a curvature radius of 12 mm and a curvature centre in the Cartesian coordinate system (15 mm, 15 mm), and a convexity with a curvature radius of 8 mm and a curvature centre in the Cartesian coordinate system (8 mm, 8 mm) (Figures 1a and 1b), the strip, after being subjected to the above thermal treatment, is adhered to the cylinder and it matches thereof external surface without showing any fracture or crack (Figures 2a and 2b) by applying a force up to 1 kg weight,

the prosthesis obtainable after thermal treatment, shaped or modelled on the dental plaster cast and cooled at room temperature, maintains the shape of the plaster cast;

the prosthesis after the thermal treatment, modelling and cooling being subjectable to further cycles of thermal treatment, modelling and cooling for at least 20 times for obtaining further prostheses.

The strip of the polymeric material constituting the model prosthesis can be obtained by moulding in a suitable mold sizes.

After the test, as said, the strip must not show any fracture and/or cracks. In other words, the strip after having adhered to the external surface of the cylinder must maintain the same features of the initial strip that is fracture-free and/or crack-free.

If the polymeric strip of the model prosthesis passes the test, i.e. it is able to mimic the concavity and con-

vexity of the cylinder on which is adhered, the model prosthesis is suitable for use as a dental prosthesis according to the present invention after being subjected to the thermal treatment, modelling and cooling as mentioned above.

Generally the force to apply the strip on the cylinder depends on the temperature and on the duration of the thermal treatment. Generally a force ranging between 0.01 and 1 Kg weight is enough to carry out the test. The force generally can be applied also by using hands.

The duration of the thermal treatment depends on the temperature. The higher the temperature the lower the time of treatment. The thermal treatment is carried out for a time comprised between 0.5 and 10 minutes preferably 1 and 5 minutes, more preferably 2 and 4 minutes.

Preferably the temperature is comprised between 110° and 180°C, more preferably 120° and 170°C for a time preferably from 1 to 5 minutes, more preferably from 2 to 4 minutes.

The thermal treatment at the indicated temperatures can preferably be carried out in oven. The thermal treatment can be carried out also in water, but in this case the treatment is carried out under pressure to reach the temperatures comprised in the above mentioned ranges.

By modelling (shaping) the model prosthesis on the plaster cast it is meant that the model prosthesis after the thermal treatment carried out for the time and at the temperature requested, is adapted onto the cast by applying a force preferably not higher than 1 kg weight. The force is preferably applied by hands. Generally modelling is carried out as soon as the thermal treatment of the model prosthesis is ended. Generally modeling is started within one minute, preferably within 30 seconds after the withdrawal of the prosthesis from the oven. Generally modelling is carried out for a time not longer than 5 minutes, preferably 2-5 minutes.

By model prosthesis, as said, it is meant any prosthesis obtainable by moulding a polymer that meets the above

mentioned test by starting from a gum plaster cast.

It is well known that prostheses can be preferably obtained with the following process:

the cast of the gum is taken by means of a metal impression tray containing a moldable material, preferably of silicone, known also as female;

in the laboratory from the female the plaster cast is obtained. Generally the plaster is poured in the cast. This forms the plaster cast;

on the cast, wax is mounted and shaped to conform the gum, then teeth are fixed, obtaining the wax prosthesis;

from the wax prosthesis the polymer prosthesis is obtained by dipping the wax prosthesis in a liquid silicone rubber, that is then hardened; after hardening wax is removed and in its place the polymer in the liquid state is poured in the hardened silicone. In this way, after polymer hardening, the model prosthesis is obtained.

The model prosthesis can also be obtained by any other process well known in the art.

Once the silicone mould is obtained, the polymeric resin in the liquid state is cast and it is let harden. In this way a copy of the prosthesis is obtained.

As said, the prosthesis, once subjected to thermal treatment, modelled according to the cast shape and cooled, maintains the cast shape. It has been surprisingly and unexpectedly found that the prosthesis thus obtained shows neither retractions (shrinkages) or dilatations. This is totally unexpected and surprising as the prosthesis is formed of both thinner and thicker sections. It is besides unexpected and surprising that also the teeth inserted in the model prosthesis do not show alterations and do not detach from the prosthesis polymer during thermal treatment and moulding of the prosthesis on the cast.

As said the prostheses of the invention can be subjected even to 20 or more cycles, even up to 50, each comprising thermal treatment, modelling on a cast and subsequent cooling after each treatment, to yield further pros-

theses having different shapes by using different casts, the latter deriving from different impressions. Therefore also the relevant casts are modified.

Therefore the prostheses obtained according to the invention can be adapted to different casts. This is an advantage as the dental arches of an individual change in the time. Furthermore each individual has a different cast.

The prosthesis after thermal treatment, modelling and cooling, being subjectable to further cycles of thermal treatment, modelling and following cooling for at least 20 times, for obtaining additional different prostheses by using casts different from that of the model prosthesis.

By polymer moulding starting from a plaster cast a model prosthesis can be obtained in a number of specimen even very high, i.e. 100 or more. The invention resides in using the model prosthesis to obtain the prosthesis according to the present claims after having subjected the model prosthesis to further cycles of thermal treatment, modelling and following cooling, to adapt the prosthesis to casts different from that of the model prosthesis.

Generally the plaster cast is obtainable from an impression that reproduces the shape of a gum as described above, or it can be prepared ex novo in a laboratory by starting from a preexisting cast and making a silicone mould as described above.

All the prostheses prepared according to the invention are new with respect to those of the prior art. The casts obtained from the dental impressions being different each from the other, as the casts used as support for shaping are obtained from unique impressions different each from the other.

The model prosthesis could also be obtained by reproducing an existing dental prosthesis by preparing a silicone mould as described above.

It has been surprisingly and unexpectedly found by the Applicant that a model prosthesis, dipped in hot water at a temperature up to 100°C, or put in an oven at the same tem-

perature, does not allow to obtain the prostheses of the invention, as a strip of the polymer of the model prosthesis so treated is not capable to reproduce the external surface of the cylinder used in the above test.

A description of the enclosed figures is herein reported.

Fig. 1a is a perspective view of the metal cylinder used in the test, the cylinder having a diameter of 30 mm and having on its lateral surface a concavity with a curvature radius of 12 mm and a curvature centre in the Cartesian coordinate system (15 mm, 15 mm), and a convexity with a curvature radius of 8 mm and a curvature centre in the Cartesian coordinate system (8 mm, 8 mm), respectively.

Fig. 1b is a sectional view perpendicular to the longitudinal axis of the cylinder used in the test of Fig. 1a.

Fig. 2a is a perspective view of the cylinder of Fig. 1a with attached the polymer strip of the prosthesis of the invention matching the surface of the cylinder including both the convexity and the concavity by applying a light pressure by hands of about 0.4 kg. A visual inspection of the strip shows that its surface does not show any fracture or crack.

Fig. 2b is a sectional view perpendicular to the longitudinal axis of the cylinder according to Fig. 1a with the strip of the polymer of the prosthesis of Fig. 2a.

Fig. 3 is a comparative figure showing a model prosthesis as applied to a plaster cast of a dental arch. From the Figure it can be seen that the model prosthesis does not reproduce the cast shape. In this comparative Figure the model prosthesis has not been subjected to heat treatment.

Fig. 4 shows the prosthesis of the invention applied to the plaster cast. It can be seen that in this case after thermal treatment of the model prosthesis, modelling on the cast and cooling at room temperature, there is a perfect matching between the plaster cast and the obtained prosthesis.

Generally the model prosthesis is substantially formed

of one or more polymers. Preferably one or more thermoplastic polymers are used provided that they meet the above test. Optionally said one or more polymers, preferably thermoplastic, can be partially crosslinked with the proviso that a strip from said polymers is such to meet the above test.

As crosslinking agents, those described further on can be used.

Additives, such as fillers, crosslinking agents, reinforcing agents, plasticizers, lubricants, stabilizers, pigments, antiadhesives, antistatic agents, anti UV, antioxidants, polymerization inhibitors, etc., can be added to said polymers.

The polymers of the present invention can be selected preferably from the classes of thermoplastic polymers. These classes are exemplified hereinafter. The thermoplastic polymers belong to the class of synthetic resins and derive from the combination of more molecules of one or more chemical compounds. The polymers can be obtained by addition polymerization or by polycondensation. By addition polymerization a reaction is meant wherein a number more or less high of molecules of one or more monomers, equal to or different from each other, bind together to form a polymer. A necessary condition for the addition reaction to take place is that the monomer contains only one unsaturation of ethylene type.

By polycondensation a reaction is meant wherein more molecules of one or more monomers having two functional reactive groups, bind together to form a macromolecule with elimination of other compounds, for example water.

The copolymers are polymers wherein the monomers are different from each other and in the polymer chain the monomeric units are distributed, more or less at random, or in a given order. In case of polymers obtained by reacting two comonomers the following types of copolymers can be formed: copolymers with random sequence when the two monomeric units are distributed at random, i.e. without a regular

distribution; block copolymers when there are blocks of rather long sequences of one monomer following those of the other monomer. Copolymers showing an alternate monomer succession are known wherein in the chain the two monomeric units follow one another alternatively. This class of polymers is formed by polycondensation reactions, but it can be obtained also by polymerization reactions, at least with long alternating sequences.

Grafted polymers, or polymers with grafts, are polymers formed of a long chain of a polymer on which polymeric chains formed of another monomer are grafted.

In polycondensation the polymer is stepwise formed. Starting from two bifunctional monomers it can be admitted that at first a simple condensation reaction among them takes place with formation of a dimer that, having two functional groups arranged respectively at the head and tail of the molecule, can react with another monomer molecule forming a trimer. This reacts with another molecule forming a tetramer, and so on, with continuous increase of the molecular weight. If high molecular weight products are desired, it is necessary that polycondensation should proceed efficiently and unrelated substances or impurities that could give rise to secondary reactions, able to interrupt chain elongation, should be not present.

Polycondensation is carried out by mixing the monomers with an optional catalyst in reactors well known for this kind of polymerization. Polymerization is carried out under controlled conditions of temperature and sometimes also of pressure.

The reaction can be carried out in an aqueous medium, in a solvent or in mass, i.e. by maintaining the compounds in the molten state. When the desired degree of polycondensation is achieved, the reaction is stopped, generally by cooling.

Polymerizations are chain reactions and generally develop as it follows: one molecule of the monomer M is activated by a catalyst (activation phase); the activated mole-

cule, that becomes very reactive, combines with another monomer molecule forming a dimer that maintains the activation and is therefore able to react with another monomer molecule forming a trimer, and so on (propagation phase). The process continues until an event takes place that deactivates the molecule (termination phase).

Chain elongation progresses very quickly as long as during polymerization, as said, an event different from that of polycondensation occurs. In fact in polycondensation the reaction proceeds with all the monomer molecules; therefore, if at a certain time the process is stopped, in the reaction mixture are found many polymeric molecules having a molecular weight slightly different from each other. On the contrary, in the polymerization the reaction mixture contains polymers together with a certain amount of monomer molecules that have not yet reacted.

The active centre triggering the start of the reaction can be an ion (cation or anion) or a radical. In fact both radicalic polymerizations and ionic (cationic and anionic) polymerizations are known.

Radical polymerization takes place when the active centre is formed of a radical, i.e. a group with a free valence, containing one electron valence or an unpaired electron. In radical polymerization three steps are distinguished: start, propagation and termination, respectively. The start or activation step takes place in the presence of a substance (catalyst) able to generate a radical. Organic peroxides and hydroperoxides show this property. When heated, they decompose originating a radical. The radical, being an unsaturated species, quickly reacts with a monomer molecule, forming a radical with an higher molecular weight. The reaction proceeds with the shifting of the unpaired electron from the radical active centre to the external carbon atom.

In the propagation step the so formed radical reacts with another monomer molecule forming a longer radical, and so on. The reaction proceeds with a quick chain increase.

The elongation of the polymeric chain does not proceed at the infinite as several events can occur, as said, interrupting the radical sequence. Such are the combination of two radicals, wherein the pairing of two terminal unpaired electrons each belonging to one of the two chains takes place; or the combination with the polymer chain of a radical deriving from the initiator.

Then the termination phase takes place.

Radicalic polymerizations can be carried out also at low temperature, by operating with initiators decomposing under the effect of energy sources different from heat. For example azodiisobutyronitrile can be used as a photoinitiator as it decomposes into radicals also at low temperatures by irradiation with ultraviolet light; redox initiators can be used, i.e. redox systems, causing the decomposition of the peroxide by means of a reducing agent. A redox system used in emulsion polymerizations is for example formed of hydrogen peroxide and F_e^{++} ions. Another example of redox initiator is formed of persulphate ion in the presence of a reducing agent as thiosulphate or bisulphite.

In cationic polymerizations the active centre is formed of a positive electric charge, i.e. a cationic group. Also in this case the reaction proceeds according to the above mentioned three steps.

In the starting step cationic polymerizations take place in the presence of initiators (catalysts) having the property of releasing easily a cation. These initiators are the so called Lewis acids as BF_3 , $SnCl_4$, $AlCl_3$, $AlBr_3$, $TiCl_4$ and some strong acids as H_2SO_4 and HF . In order to start polymerization the Lewis acids require the presence of a co-catalyst such as water, alcohol, acetic acid.

In the propagation step the formed ion reacts with another monomer molecule giving a dimer cation and so on. The reaction quickly proceeds by adding further monomer molecules obtaining one polymer ion.

The termination phase occurs because various events take place that stop polymerization, in particular the fol-

lowing ones: the transfer of one proton from the polymer to a monomer molecule, starting the formation of a new polymeric chain, or the transfer of a proton from the polymer to the anion of the catalyst.

Differently from the radical process, the cationic process allows to carry out very quick polymerizations even at very low temperatures, obtaining in a few seconds a molecular weight of some millions.

In anionic polymerizations different monomers can be polymerized in the presence of substances generating an anion initiator, such as for example sodium amide NaNH_2 , potassiumamide KNH_2 or alkyl metals. The reaction starts with the formation of a negative ion from the catalyst, the anion then reacts with a first monomer molecule and the propagation phase then starts.

The polymerization is carried out in an homogenous or heterogeneous phase: in an homogeneous phase according to the mass and solution polymerization, in an heterogeneous phase according to emulsion and suspension polymerization.

In mass polymerization gaseous monomers and liquid monomers (for example methyl methacrylate, styrene) are polymerized without addition of solvents and by operating in the presence of the catalyst under suitable conditions of temperature and pressure.

In solution polymerization the monomer is dissolved in a solvent and the catalyst is added to this solution. At the end the polymer can be separated by evaporating the solvent together with the unreacted monomer, or by precipitating the polymer by adding a suitable coagulating agent.

In emulsion polymerization the monomers insoluble in water such as for example vinyl monomers, styrene, etc., are polymerized in an aqueous emulsion in the presence of suitable emulsifying agents. The monomer is mixed with water and the emulsifying agent is added so that a monomer aqueous emulsion is formed. As initiators peroxides or redox initiators are used. At the end of polymerization a polymer emulsion, called latex, is obtained, from which the

polymer can be recovered by coagulation by adding an electrolyte. In this system the reaction proceeds under substantially isothermal conditions, as sufficient amounts of water are present to disperse the reaction heat; furthermore high polymerization speeds, high and reproducible molecular weights, are obtained.

The polymerization in suspension or in beads (powder) takes place when the emulsifying agent is in a reduced amount or it is absent. In these cases an aqueous suspension is obtained. The monomer collects in beads having a larger diameter than in the case of the emulsion oily particles. The bead sizes can also be of the order of some millimeters, and are kept in suspension by mechanical stirring. In order to avoid beads sticking one to the other, small amounts of stabilizers, as for example gelatine, starch, bentonite, are added.

At the end of polymerization a product in the form of regular beads, easily separable from the aqueous suspension, is obtained. The reaction proceeds with a lower speed than emulsion polymerization, but there is the advantage to obtain highly pure polymers, as in emulsion polymerization the product always contains impurities due to the several auxiliary substances being introduced.

The polymerization process has a statistical nature since not all the monomer molecules polymerize with the same speed and the formed polymeric chains have not the same length. For this reason the obtained resins are never formed of only one chemical compound but of a mixture of polymeric chains having a different polymerization degree. As many physical and chemical properties depend on the polymerization degree, it is sometimes necessary to carry out a separation or fractionation to separate the obtained product into fractions each having molecular weights comprised in a limited range, or to isolate the fraction having the desired molecular weight. In polymer fractionation the principle is usually applicable that generally the solubility in a given solvent decreases with increasing mo-

molecular weight. The method consists in a fractional precipitation from a diluted solution of the polymer, by using as precipitating agent a non-solvent agent. In this way the less soluble fractions, those having a higher molecular weight, are preferably precipitated.

Another method for polymer fractionation consists in mixing the product obtained from polymerization with a solvent favouring the solubilization of the low molecular weight fractions. This method is called fractionatal extraction.

Even if various synthetic resins share, for example a same molecular weight, however they have a combination of properties that allow to differentiate them and address them to different uses and specific applications.

Plastic materials are produced under the form of powders or granules, tablets, beads, pellets, etc. For the preparation of the various plastic articles (moulding) they are mixed with some auxiliary ingredients, then moulded by using different equipments in relation to the type and the article to be prepared.

The auxiliary ingredients are substances added and mixed with the resins before moulding, and sometimes they are already incorporated in the moulding powders. The auxiliary ingredients comprise the above indicated additives herein described in more detail.

The fillers or charges are used to improve the mechanical and electric properties. They are used in amounts up to 50% by weight of the formulation. Fillers are both organic and inorganic compounds. Among the former, wood flour, cotton, jute or cellulose fibers (meth)acrylic polymers; among inorganic fillers diatomaceous earth, mica, graphite, glass, can be mentioned. The organic fillers improve some mechanical properties, in particular resilience, while they slightly worsen tensile and flexural strength and are uninfluent on heat resistance and electric properties. The inorganic fillers, except those having a fibrous structure, markedly worsen the mechanical properties

but improve electric and thermal properties. Fillers are rarely used in thermoplastic resin technology.

The reinforcing agents are materials having a fibrous structure, such as cotton, but above all glass fibers, felt, short fibers, fabrics, etc. With the reinforcing agents the so called reinforced plastic materials and plastic laminates are prepared, wherein these additives act as a support for the resin and remarkably increase the mechanical properties thereof.

Plasticizers are used in thermoplastic polymers for reducing rigidity and increase flexibility thereof. The plasticizers most commonly used are for example phosphates of higher alcohols, such as trioctylphosphate and tricresylphosphate, or glycerine esters such as the corresponding diacetate and triacetate, esters of polyethyleneglycols, oleates, stearates, ricinoleates. Mixtures of plasticizers are generally used.

Lubricants are used in order to improve the sliding characteristics of thermoplastic polymers and thus to make it easier thereof processing. As lubricants metal soaps, for example calcium, zinc, magnesium stearates and oleates, or amyl and butyl stearates, are used. The amounts of these additives are generally lower than 1% by weight.

Stabilizers are additives which prevent or limit resin degradation due to agents as light, heat, oxygen. Generally metal soaps are used, wherein the organic acid is usually selected from the following: stearic, lauric, ricinoleic, benzylic acid and phenol. The cation is generally a metal selected from the following: barium, cadmium, calcium lead, tin, zinc. In order to maintain resin transparency, organic phosphites are added. Also stabilizers different from soaps and totally organic can be used, in particular substances containing epoxy groups.

Plastic materials can be coloured with pigments or with organic dyestuffs dissolved or dispersed in the plastic mass during processing. The dyestuff must have specific properties, such as easy dispersibility in the resin, ther-

mal stability, light stability, toxicity free.

Other additives that can be used are antiadhesives, which are directly applied by brushing or by spraying onto the mould surface to make it easier the detachment of the moulded article. Examples of antiadhesives are silicone oils and cellulose resins, that are applied in films or in thin layers by painting.

Hardening agents are catalysts added when the polymerization must take place or be completed at the application site.

Crosslinking agents are generally crosslinking comonomers added during polymerization. These comonomers, containing at least two double bonds, are added in amounts comprised between 0 and 2%, preferably between 0 and 1% by weight with respect to the total monomer amount. Examples of crosslinking comonomers are ethylenglycol di(meth)acrylate, di-, tri-, tetraethylenglycol di(meth)acrylate, 1,3-1,4-butylenglycol di(meth)acrylate, 1,6-hexandiol di(meth)acrylate, 1,9-nonandiol di(meth)-acrylate, divinylbenzene, trivinylbenzene, allyl (meth)acrylate, diallyl maleate, diallyl fumarate, triallyl cyanurate, pentaerythrol triacrylate; trimethylolpropane tri(meth)-acrylate, etc. In case of acrylic polymer, (meth)acrylic acid, glycidol (meth)-acrylate, (meth)acrylamide can be used as crosslinking agents.

The processing of moulding thermoplastic powders is carried out by loading them onto the mould and then heating so that the powders melt and become fluid, until filling all the mould cavities. Before discharging from the mould the resin is cooled and solidified.

In injection moulding the resin is loaded by a hopper; the resin is compressed by a piston and thus get heated. The resin is softened and loaded onto a mould and takes thereof shape while cooling.

Among the plastic materials obtained by polycondensation the following ones can for example be mentioned. Polyester resins derive from the polycondensation of acids

with alcohols. There are several kinds of polyester resins. For example, saturated polyesters, in general, that are obtained by condensation of bicarboxylic saturated acids with a saturated bivalent alcohol. The acid can be selected for example from the following: saturated acids, for example phthalic acid and isophthalic acid; the alcohol can be selected from ethylene glycol, propylene glycol or butylene glycol.

Long chain aliphatic saturated acids can also be used. Glycols having a longer chain, such as dipropylene glycol and triethylene glycol can also be used.

Epoxy resins are prepared by polyaddition of an epoxide, in general epichlorohydrin, with a phenol. The epoxy groups react again with phenol and epichlorohydrin and then the reaction proceeds up to the formation of polymers having a linear structure and high molecular weights. By varying the operating conditions the molecular weight can be adjusted, obtaining products having a low polymerization degree (liquid resins) or a high polymerization degree (solid resins). Epoxy resins are therefore linear and thermoplastic; thereof chains however contain a great number of very reactive groups, hydroxyl groups -OH and epoxy groups. The chains can therefore react with each other or with other bifunctional compounds to form high molecular weight tridimensional insoluble complexes that do not melt and show a high hardness. This is obtained by adding suitable substances, called hardening agents, which can be of two types: catalytic hardeners that catalyze only the reaction between two epoxy groups, and reactive hardeners which instead take an active part in the process. Catalytic hardeners are for example tertiary amines and boron trifluoride. These substances are able to cause an ionic polymerization among epoxy groups. Reactive hardeners are in particular primary and secondary amines, organic acids, i.e. substances able to react with both hydroxyl groups and epoxy groups.

Other resins originating from polycondensation processes are for example polyurethane resins.

Polyurethane resins are prepared from alkyl diisocyanates by reaction with glycols, to obtain thermoplastic linear polyurethanes. An example of a glycol that can be used is butylene glycol. The most used isocyanates are for example phenylene diisocyanate and hexamethylene diisocyanate. Plastic materials obtained by polymerization reaction preferably comprise acrylic resins, obtained from the polymerization of vinyl monomers.

By the terms acrylic resins, polyacrylic resins, acrylic (co)polymers, polymers obtained by using as monomers the derivatives of the acrylic and methacrylic acids, such as for example alkyl (meth)acrylates, acrylic nitriles, etc., separately or in admixture with each other, are meant.

The polymerization of acrylic esters is carried out in mass, in suspension or in aqueous emulsion. As catalysts organic peroxides or potassium or ammonium persulphate and hydrogen peroxide are used.

The polymerization in mass is carried out by heating the monomer in the presence, for example, of benzoyl peroxide. The mass is then poured in moulds wherein polymerization is completed. After cooling, the manufactured article is discharged.

In order to obtain moulding powders, polymerization is carried out in aqueous suspension in the presence of peroxides, for example benzoyl peroxide; the formed beads are separated by centrifugation or filtration, then mixed with additives and milled.

Emulsion polymerization can be used to obtain acrylic resins as moulding powders.

The manufactured articles based on polymethacrylic resins have a high transparence, a remarkable mechanical and chemical resistance, and can be coloured with colorants.

More specifically acrylic (co)polymers derive from polymerizable monomers and can be obtained, as said, by polymerizing polymerizable suspensions of said monomers.

Fluid suspensions can be prepared by mixing

a) a liquid base formed by at least one polymerizable mono-

mer,

b) a filler,

wherein the filler can be an organic or mineral compound.

Organic fillers are for example polymers, preferably (meth)acrylic polymers.

An example of fluid suspension comprising an inorganic filler is the following:

a) a liquid base formed by at least one polymerizable monomer,

b) a finely milled mineral filler,

c) a silanizing agent of the mineral filler,

d) an hydrolysis catalyst of the silanizing agent selected from ammonium salts of organic acids.

Details of the components of the suspensions are given herein below.

Polymerizable monomers are selected from alkyl or hydroxyalkyl esters of acrylic or methacrylic acid wherein the alkyl group contains from 1 to 8 carbon atoms, preferably from 1 to 6 carbon atoms, or amides, and mixtures thereof. Examples of said esters are methyl(meth)acrylate (MMA), ethyl(meth)acrylate, propyl (meth)acrylate, butyl(meth)acrylate, tert-butyl(meth)acrylate, sec-butyl(meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate, (meth)acrylamide.

To the monomer or to the mixture of acrylic monomers, another monomer can optionally be added, having only one double bond polymerizable by radicalic route, in an amount in general not higher than 80%, preferably not higher than 50% by weight, such as for example, styrene, alpha-methylstyrene, (meth)acrylonitrile, N-alkyl or N-arylmaleimides, having respectively an alkyl from 1 to 10 carbon atoms and an aryl from 6 to 12 carbon atoms.

The preferred acrylic (co)polymers are those containing methylmethacrylate for at least 70% by weight and methylmethacrylate copolymers with esters of the acrylic acid, preferably ethyl or methyl acrylate.

Methylmethacrylate is particularly preferred. It can

be used alone to yield polymethylmethacrylate or in admixture with other vinyl monomers. As vinyl monomers, styrene, alpha-methyl styrene, etc., can be mentioned.

In the polymerizable compositions mineral fillers can be used, as inorganic substances having hydrophilic surfaces characterized by the presence of polar groups, preferably of hydroxyl type, capable to react with a silanizing agent present on the filler. As inorganic fillers, amorphous and crystalline silica (quartz, cristobalite, etc.), glass, alumina, trihydrate aluminum, calcium carbonate, mineral silicates, alumino silicates (mica, talc, wollastonite, etc.) mineral oxides as Fe_2O_3 , TiO_2 , etc. can be mentioned. It is preferred that the filler particles have a granular or spheroidal shape. The average diameter of the particles is generally comprised between 0.1 and 50 μm and the surface area between 0.5 and 10 m^2/g . Generally the amount of mineral filler to be used in the compositions depends on the desired characteristics of the final manufactured articles and on the fluidity property of the suspension.

Generally the amount of fillers, expressed as percent by weight, ranges from 30 to 80% on the total suspension. The remaining part is formed of polymerizable monomers.

The silanizing agent is an organic derivative of silicon containing hydrolysable groups.

The silanes that can be used are for example the following: methyltriethoxysilane, methyltrimethoxysilane, vinyltriethoxysilane, γ -methacryloxypropyltrimethoxysilane, γ -methacryloxypropyltris(2-methoxyethoxy)silane, γ -glycid-oxy propyl-trimethoxysilane, γ -mercaptopropyl triethoxysilane, γ -aminopropyltriethoxysilane, N- β {aminoethyl} γ -amino propyltrimethoxysilane, etc.

The silane hydrolysis catalyst is selected from ammonium salts of organic acids having general formula



wherein R_4 is a hydrogen atom or an alkyl, cycloalkyl, alkylaryl, optionally unsaturated, radical $\text{C}_1\text{-C}_{20}$, R_5 , R_6 , R_7 , R_8 ,

equal to or different from each other, can be hydrogen or alkyl or cycloalkyl C₁-C₂₀ radicals. Examples of catalysts are isopropylammonium acetate, isopropylammonium methacrylate, ammonium oleate, ammonium stearate, ammonium methacrylate, n-propylammonium methacrylate, dimethylammonium butyrate, isopropylammonium oleate, isopropylammonium benzoate, ethylammonium acrylate, etc.

The silane compound is used at concentrations from 0.01% to 2% by weight with respect to the filler and the catalyst between 0.01% and 1% by weight with respect to the whole composition weight.

To the suspension surfactants soluble in the monomer and having suitable affinity with the mineral filler can also be added. Generally, surfactants containing ethoxy or propoxy groups such as ethoxylated alkylphenols, sulphonates, alkyl sulphates, phosphates and alkylammonium phosphonates, wherein the alkyl group has up to 20 carbon atoms, phosphoric esters, etc., are used. Examples of surfactants are ethoxylated nonylphenol containing from 1 to 15 ethylenoxide molecules, ethoxylated octylphenol containing from 1 to 15 ethylenoxide molecules, ammonium dodecylbenzenesulphonate, sodium 2-ethylhexylsulfosuccinate, ammonium and laurylalcohol ethoxylated, with 1-3 ethylenoxide molecules sulphate, C₄-C₁₂ alcohol phosphates, acid phosphates of stearamidopropyldimethyl-β-hydroxy ethyl-ammonium, etc. The surfactant amount is in the range 0-0.5% by weight with respect to the whole composition weight, preferably 0.05-0.2%.

To the polymerizable suspension other additives can be added, in particular pigments and/or inorganic and/or organic dyestuffs, in amounts between 0 and 5% by weight on the total; agents to ease detachment from the moulds, anti-static agents, plasticizers, anti UV agents, antioxidants, polymerization inhibitors, etc. in amounts between 0 and 2% by weight on the total. See for example those mentioned above.

The viscosity of the suspension can be increased and

brought to the optimum level for injection moulding or for mass polymerization by addition of viscosity modifiers, such as for example methacrylic or vinyl homo and/or copolymers. Generally compounds having a high molecular weight are used; for example polymers or copolymers with average molecular weight (Mw) comprised between 20,000 and 1,000,000, and preferably between 50,000 and 500,000.

Examples of viscosity modifier polymers are polymethylmethacrylate, methylmethacrylate-methylacrylate copolymers, methylmethacrylate-styrol copolymers, methylmethacrylate-butylacrylate copolymers, polyethylmethacrylate, methylmethacrylate-methacryloxypropyltrimethoxy silane, etc.

Generally the viscosity modifiers are added in an amount by weight not higher than 20% with respect to the monomer, preferably 0.5-10%.

The transformation into manufactured articles of the polymerizable suspensions can be carried out by moulding by applying a pressure comprised between 1 and 4 atm and at temperatures from 70° to 100°C for closed moulds, upon previous addition of a catalyst, preferably peroxidic, in amounts generally in the range from 0.1 to 2% by weight. Examples of these catalysts are benzoylperoxide or t-butylcyclohexylperoxycarbonate.

Optionally agents to favour the detachment from the moulds, such as for example stearic acids, glycerine monostearate, etc., can be added.

Before moulding it is advantageous to deaerate the suspension under stirring by operating under a reduced pressure.

By using milder polymerization conditions and suitable thermal cycles, it is possible to polymerize the suspension with techniques similar to those used for the production of cast methacrylic plates.

As polymers for preparing the prostheses of the present invention also acrylic (co)polymers having good mechanical properties can be used. These polymers are pre-

pared by using compositions based on acrylic (co)polymers having shock-resistant properties, such as for example described in EP 270,865, USP 3,985,703. These flexible materials, in particular those described in the EP patent, are obtained by mixing acrylic (co)polymers with a shock-resistant additive in an amount equal to 20% by weight or even higher. Examples of compounds used as shock-resistant additives are for example core-shell emulsions having a resin core, an intermediate layer of acrylic rubber and an external layer of (meth)acrylic resin. The core can be formed for example of a crosslinked acrylic polymer and the intermediate layer is formed of a crosslinked elastomeric copolymer having a Tg lower than 25°C, preferably lower than -10°C; the external layer is formed of (meth)acrylic resin grafted to the rubber.

A typical composition of shock-resistant acrylic (co)polymers comprises:

- 40 - 95% by weight of a thermoplastic resin formed of acrylic (co)polymers,
- 60 - 5% by weight of a polymer having a multilayer structure comprising:

5 - 60% by weight of a central core of thermoplastic acrylic resin as defined,

20 - 50% by weight of a first layer surrounding the central core, constituted by a crosslinked elastomer butyl acrylate/styrene 85/15.

13 - 35% by weight of an acrylic resin forming the external layer. The sum of the components being 100%.

As shock-resistant additives of acrylic (co)polymers elastomers having a very low Tg can be used. In this way in the compounding phase it is possible to use amounts of additive lower than the above indicated 20%.

Acrylic copolymers as described above having abrasion resistance comparable with that of acrylic (co)polymers can also be used. They can be used for example in the following compositions:

- from 70% to 99.5% by weight, preferably from 80% to

99%, still more preferably from 90 to 98% by weight, of a thermoplastic resin based on acrylic homopolymers or copolymers as defined above wherein at least 20% by weight, preferably at least 50% by weight is formed of (meth)acrylic monomers.

- from 0.5% to 30% by weight, preferably from 1 to 20%, still more preferably from 2 to 10% by weight of an elastomer, preferably crosslinked, having a Tg on-set vitreous transition temperature (ASTM D 3418-75) lower than 0°C, preferably lower than -5°C, still more preferably lower than -10°C,

the elastomeric component being dispersed in the acrylic resin as spherical particles and/or elongated particles having diameter, measured by electronic microscopy (TEM transmission electronic microscopy), comprised between about 10 nm and about 2,000 nm, the particles of the elastomeric component optionally including acrylic resin particles.

The sum of the components being 100%.

The preferred acrylic (co)polymers of the thermoplastic resin are those containing methylmethacrylate for at least 70% by weight, as PMMA and methylethacrylate copolymers with (meth)acrylic acids or esters thereof, preferably ethyl, methyl, butyl acrylate or (meth)acrylic acid.

The elastomers are obtainable for example by polymerizing one or more (co)monomers selected from the following groups:

- acrylic acid esters wherein the alkyl group has from 1 to 16 carbon atoms, preferably from 2 to 12 carbon atoms, such as ethyl acrylate, propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, etc.,
- alkoxy-alkyl acrylates, wherein the total number of the carbon atoms between the alkyl group and the alkoxy group is in the range 2-16, preferably 3-15; such as for example 2-methoxyethyl acrylate,
- monomers having a double ethylenic unsaturation for

example butadiene or substituted butadiene such as for instance isoprene, chloroprene, 2-3 dimethylbutadiene, - vinyl monomers, for example styrene and derivatives thereof, such as for example methyl- and ethyl-styrene, wherein the alkyl group is in ortho or para position; α -methylstyrenes; mono-, di-, tri-, tetra-, penta-halogenostyrenes, wherein the halogen is selected from Cl, F; said monomers being in amounts not higher than 40% by weight, preferably not higher than 30% by weight on the total amount of the monomers of the elastomeric component.

The preferred elastomer is the copolymer of butyl or 2-ethylhexyl or octyl acrylate containing styrene in amounts comprised between 5 and 30% by weight, preferably between 10 and 20%.

The compositions under the form of beads can be prepared by a suspension polymerization process comprising the following steps:

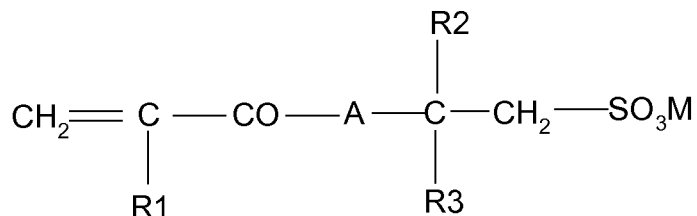
- 1) preparation of elastomer beads by a suspension polymerization process of the monomers, optionally in the presence of at least one crosslinking monomer;
- 2) polymerization in the same polymerization suspension containing the elastomer beads obtained in step 1), of (co)monomers of the acrylic polymer, said (co)monomers being selected from those indicated above.

A preferred process for suspension polymerization, preferably aqueous suspension polymerization, of the above monomers is carried out in the presence of a radical initiator soluble in the monomers and of a suspending agent to stabilize the suspension. For example inorganic and organic suspending agents can be mentioned. Among the latter, polymeric organic compounds such as polyvinylalcohol, acrylic copolymers containing a (meth)acrylic acid, carboxymethyl-cellulose etc., can be mentioned.

The beads obtained with the above described suspension polymerization process, after washing with water and drying, are compounded (see above), preferably by extrusion, in order to obtain granules.

As preferred suspending agents the following are mentioned:

- homopolymers of a compound of formula



(I)

wherein R1 = H or CH₃; R2 and R3, equal to or different, are H or C₁-C₈ alkyls optionally branched when possible; M is an alkaline or alkaline-earth metal or ammonium and A is NH, oxygen or NCH₃,

- copolymers of the compound of formula (I) with acrylic monomers in amounts not higher than 40% by weight.

Generally the amount of the suspending agent is in the range 0.1 - 1.5%, preferably 0.2 - 1% by weight, referred to the total weight of the aqueous phase.

In the aqueous suspension polymerization for the preparation of the elastomer (step 1) of the process, ratios by weight between the aqueous phase and the monomers generally comprised between 1.5:1 and 20:1, preferably from 2:1 to 10:1 are used, in the presence of a radical polymerization initiator soluble in the monomer. The presence of a chain transfer agent is not requested. The reaction temperatures are those at which the initiator decomposition occurs, and are generally comprised between 50°C and 120°C.

In the aqueous suspension polymerization for the preparation of acrylic (co)polymers (step 2) of the process, aqueous phase/monomers ratios by weight generally comprised between 1:1 and 10:1, preferably between 1.4:1 and 6:1, are used in the presence of a chain transfer agent and a radical polymerization initiator, both selected from those soluble in the monomer. The reaction temperatures are those at which the initiator decomposes and are generally in the range 50°C-120°C.

As radical initiators, peroxides such as for example dibenzoylperoxide, t-butylperoxydiethyl acetate or unstable azocompounds, such as for example azodiisobutyronitrile, can be mentioned.

As chain transfer agents, alkylthiols with a linear or when possible branched alkyl group C₃-C₂₀, preferably C₄-C₁₂ such as for example n-butanthiol, n-octanthiol, n-dodecanthiol, ter-dodecanthiol, cyclohexanthiol, pinanthiol, can be used.

The preferred suspending agents of formula (I) or their copolymers with acrylic monomers are described in patent application EP 457,356 herein incorporated by reference. In particular the suspending agents of formula (I) can be, for example, sodium 2-(meth)acrylamido-2-methylpropansulphonate, sodium 2-acrylamidopropan-sulphonate, sodium 2-acrylamido-2-ethansulphonate.

The acrylic monomers that can be copolymerizable can be for example (meth)acrylamide, alkaline or alkaline-earth salts of the (meth)acrylic acid, (meth)acrylic acid esters with a C₁-C₄ aliphatic alcohol, acrylonitrile.

For the crosslinking of these polymers, crosslinking comonomers containing at least two double bonds, in the amounts indicated above, can be added in polymerization. Examples of crosslinking comonomers are ethylenglycol di(meth)acrylate, di-, tri-, tetraethylenglycol di(meth)acrylate, 1,3- 1,4-butylenglycol di(meth)acrylate, 1,6-hexandiol di(meth)acrylate, 1,9-nonandiol di(meth)acrylate, pentaerythrol triacrylate, trimethylolpropane tri(meth)acrylate etc.

Crosslinking agents containing a functional polar group can also be used in a percentage from 0 to 2% by weight on the total weight of the monomers; examples of these monomers are (meth)acrylic acid, glycidyl (meth)acrylate, (meth)acrylamide.

In the case of acrylic (co)polymers, crosslinking can also be carried out without addition of a crosslinking monomer when acrylic esters are used as comonomers, wherein

the alkyl has a number of carbon atoms higher than or equal to 4, preferably C₄-C₁₀, for example butyl acrylate, 2-ethylhexyl acrylate, n-octyl acrylate.

The polymers used for preparing the prostheses of the present invention meet the requirements established by the sanitary regulations for their clinical use, in the first place absence of toxicity.

The prostheses of the present invention preferably comprise, or are formed of, acrylic (co)polymers, preferably the acrylic polymer used to prepare the model prostheses on the market, i.e. the prostheses that have not been treated according to the process of the present invention.

A preferred process for preparing the prostheses of the present invention is carried out by mixing an acrylic (co)polymer in powder form, for example polymethylmethacrylate (PMMA) alone or in admixture with other acrylic polymers, with a liquid acrylic monomer, for example methylmethacrylate (MMA).

The powder contains, besides the polymer, a plasticizer different from phthalate, initiators such as for example peroxides, and pigments.

The liquid, in addition to MMA, contains a crosslinking agent, for example ethylenglycol dimethacrylate and a catalyst, for example a peroxide, see also above for these components.

A product available on the market has the following composition (% by weight)

Powder: polymethylmethacrylate 95.5, plasticizer (different from phthalate) 3.8, initiators 0.6, pigments 0.1.

Liquid phase: methylmethacrylate 95.9, crosslinking agent 4.0, catalyst 0.1.

By mixing the two components a swelling at first occurs and then an homogeneous malleable mass is formed that, however, depending on the amounts of the components and of the mixing time, has a varying consistency. Mixing is carried out for a time not longer than 30 seconds, preferably lower than 10 seconds.

Preferably the process is carried out at temperatures in the range from 70°C to 40°C or lower and, if desired, also down to room temperature. Preferably pressure is applied, generally not higher than 5 atm and not lower than 2 atm, preferably between 4 and 2 atm. The weight ratios powder/liquid are generally from 1 (powder) : 1 (liquid), up to 4:1, preferably 1:1 to 2:1.

The polymerization time depends on the temperature and pressure used. Generally it is lower than one hour, preferably not longer than 30 minutes. For example, by operating at 4 atm at 40°C, the polymerization time is about 15 minutes.

A further object of the present invention is a process for preparing dental prostheses comprising the following steps:

- a) heating a model prosthesis, as defined above, at a temperature in the range 105°C-250°C, under atmospheric pressure,
- b) transferring the prosthesis on a dental plaster cast of a dental arch,
- c) modelling the prosthesis on the dental plaster cast by adapting it to the shape of the dental plaster cast, by applying a force preferably lower than 1 kg weight, preferably by hands,
- d) cooling at room temperature.

The obtained prosthesis can be subjected to further processes comprising steps a)-d), by using different plaster casts of dental arches, for at least 20 times, in order to obtain other prostheses of different shapes.

By room temperature it is meant a temperature in the range 15° - 25°C.

In step a) the heating time is generally comprised between 0.5 and 10 minutes, preferably 1 - 5 minutes, more preferably 2 - 4 minutes.

In step a) preferably temperature is in the range 110°-180°C, more preferably 120°-170°C; the heating time preferably ranges from 1 to 5 minutes, more preferably from

2 to 4 minutes.

In step b) the prosthesis is transferred on the plaster cast of a dental arch immediately after the end of the heating step a), preferably in a time not higher than 1 minute, more preferably in a time not higher than 30 seconds.

In step c) the force applied is preferably comprised between 0.1 and 1 Kg weight.

In step d) the prosthesis is preferably allowed to cool in air down to room temperature.

A further object of the present invention is the use of the dental prostheses of the invention obtainable from the model prosthesis according to the above described process, to obtain other prostheses by subjecting the prostheses of the invention to steps a)-d) of the above described process (i.e. a treatment cycle), but using in step c) each time a different plaster cast.

The following examples are given for illustrative purposes and are not limitative of the present invention.

EXAMPLES

Test of the polymeric material of the model prosthesis

A strip 6X6X80 mm of the polymeric material forming the model prosthesis, takes the external form of a metal cylinder having a diameter of 30 mm and a concavity with a curvature radius of 12 mm and a curvature centre in the Cartesian coordinate system (15 mm, 15 mm), and a convexity with a curvature radius of 8 mm and a curvature centre in the Cartesian coordinate system (8 mm, 8 mm) (Figs. 1a and 1b). The strip, after being subjected to the thermal treatment at temperatures in the range 105°C-250°C under atmospheric pressure, by applying a force up to 1 kg weight is let adhere to the cylinder and it reproduces the external surface thereof without showing any fracture or cracks.

EXAMPLE 1

A composition for prosthetic bases is used, formed of two components: a powder, essentially constituted by an acrylic polymer and a liquid, essentially constituted by an acrylic monomer. The composition is commercialized with the trade-

mark Sintodent®.

1.1

Preparation of the strip for testing the polymer to be used in the prosthesis preparation

The two components of the composition are mixed in a ratio by weight solid component/liquid component of about 1.4. It is noticed that after mixing the mixture swells and a malleable mass like a paste is obtained. Mixing is carried out with a spatule for 5 seconds. The mould reproducing the form of a strip 6X6X80 mm is filled with the malleable mass by the aid of a spatule. The mould is heated for 15 minutes at 40°C under a pressure of 4 atmospheres. It is let cool at room temperature and the strip is removed from the mould.

The obtained specimen is subjected to thermal treatment at 140°C for 4 minutes under atmospheric pressure in an oven and is then submitted to the above described test.

Within 30 seconds from the end of the thermal treatment, the strip is applied to the cylinder lateral surface by the aid of a light pressure by hands of about 0.4 kg weight (4 Newton). It is observed that it perfectly matches the surface of the cylinder. The test results are shown in Figs. 2a and 2b.

The test is therefore passed and the polymer is suitable for preparing a dental prosthesis.

1.2

Preparation of the dental prosthesis

30 g of powder (acrylic polymer) and 22 g of liquid (methylmethacrylate monomer) of the commercial product Sintodent® are mixed for 5 seconds until obtaining an homogeneous liquid mass. The liquid mass is poured in a muffle filled with gelatine or silicone to obtain the counter-mould. The liquid resin is poured in the muffle through an opening at the top of the mould until the slurry does not come out from the hole for the air vent located at the same height of the opening. Polymerization is carried out in a pressure cooker for 15 minutes at 40°C under a pressure of

4 atm.

The mixture is let cool at room temperature and the prosthesis is removed from the muffle.

This prosthesis is then used for a different plaster cast of a dental arch. Fig. 3 shows the prosthesis laid on the plaster cast before the thermal treatment. By subjecting the prosthesis to the same thermal treatment of the strip in an oven, the prosthesis becomes malleable on the different plaster cast. After cooling in the air, it is found that the hollow part of the prosthesis reproduces exactly the shape of the plaster cast. Fig. 4 shows the prosthesis of the invention moulded on the plaster cast.

The prosthesis obtainable after thermal treatment and cooling in air, does not show retractions or dilatations with respect to the plaster cast, as shown in Fig. 4.

1.3

Use of the prosthesis obtained in Example 1.2 (shown in Fig. 4) subjected to an additional thermal treatment and moulding on a plaster cast different from that of Fig. 4.

The prosthesis obtained in example 1.2 has subjected to a further thermal treatment at 140°C for 4 minutes under atmospheric pressure and moulded on a plaster cast obtained from a different dental arch, then cooled at room temperature.

The so obtained prosthesis according to the present invention perfectly matched the plaster cast shape and did not show any retraction or dilatation with respect to the plaster cast.

1.4

Example 1.3 has been repeated by using each time a different plaster cast deriving from a different impression for a total of 20 times. The obtained results are in line with those obtained in example 1.3: the prosthesis exactly fits the cast in all the tests carried out and does not show any retraction or dilatations with respect to the plaster cast.

EXAMPLE 2

The polymer of example 1 is used and example 1.2 is re-

peated for preparing a prosthesis according to the present invention but using a thermal treatment at 180°C and for a time of three minutes under atmospheric pressure.

Immediately after thermal treatment (30 seconds) the prosthesis was moulded on the plaster cast of example 1.2, a light pressure of about 0.4 kg weight has been applied by hands. It has been found that the so obtained prosthesis perfectly fits the plaster cast used in example 1.2 and does not show any retraction or dilatation with respect to the plaster cast.

2.1

Example 2 has been repeated but using another plaster cast different from that of example 1.2.

It has been found that the so obtained prosthesis perfectly fits the new plaster cast and does not show any retraction or dilatation with respect to the new plaster cast.

Example 3 comparative

Example 1 has been repeated but subjecting the strip to thermal treatment in oven at the temperature of 90°C under atmospheric pressure. The time of treatment at 90°C was of 9 minutes.

The strip is submitted to the above test and a force of about 1 kg weight is applied using the hands for moulding the strip on the cylinder.

It is noted that the strip maintains its initial shape, it does not bend and therefore it cannot be conformed to the surface of the cylinder. Therefore the test is not passed.

This example shows that the polymer being used, subjected to the indicated thermal treatment, does not allow to obtain the prosthesis of the invention.

EXAMPLE 4 comparative

Example 3 has been repeated but by applying a force of 10 kg weight for moulding the strip on the cylinder.

It is observed that the strip maintains its initial shape, it does not bend and therefore cannot be adapted to the surface of the cylinder. Furthermore it is noted that during modelling in the strip cracks start to form. In order

to avoid breaking of the sample, the test is interrupted. This example shows that the polymer being used, subjected to the indicated thermal treatment, even by increasing of about 10 times the force applied to the strip with respect to example 3 comparative, does not allow to obtain the prosthesis of the invention.

CLAIMS

1. Dental prostheses obtainable starting from a model prosthesis, obtainable by polymer moulding onto a dental plaster cast, and subjecting the model prosthesis to thermal treatment at temperatures in the range 105°C-250°C under atmospheric pressure, the model prosthesis satisfying the following test:
a strip 6X6X80 mm of the polymeric material that forms the model prosthesis takes the external form of a metal cylinder having a diameter of 30 mm and a concavity with a curvature radius of 12 mm and a curvature centre in the Cartesian coordinate system (15 mm, 15 mm), and a convexity with a curvature radius of 8 mm and a curvature centre in the Cartesian coordinate system (8 mm, 8 mm), the strip, after being subjected to the above thermal treatment, is adhered to the cylinder and it matches thereof external surface without showing any fracture or cracks by applying a force up to 1 kg weight,
the prosthesis obtainable after thermal treatment, shaped on the dental plaster cast, cooled at room temperature maintains the shape of the dental plaster cast, the prosthesis after the thermal treatment, modelling and cooling being subjectable to further thermal treatment, modelling and following cooling cycles for at least 20 times to obtain further prostheses.
2. Dental prostheses according to claim 1, wherein the force applied in the test is comprised between 0.01 and 1 kg weight.
3. Dental prostheses according to claims 1-2, wherein the thermal treatment is carried out for a time from 0.5 to 10 minutes.

4. Dental prostheses according to claim 3, wherein the thermal treatment is carried out for a time from 1 to 5 minutes.
5. Dental prostheses according to claims 1-4 wherein the temperature of the thermal treatment is in the range 110°-180°C for a time from 1 to 5 minutes.
6. Dental prostheses according to claim 5 wherein the temperature of thermal treatment is in the range 120°-170°C for a time from 1 to 5 minutes.
7. Dental prosthesis according to claims 1-6 wherein the model prosthesis is prepared from a silicone mould of a dental prosthesis.
8. Dental prostheses according to claims 1-6, wherein the model prosthesis is formed by one or more polymers.
9. Dental prostheses according to claim 8 wherein the polymers are thermoplastic polymers.
10. Dental prostheses according to claims 8-9 wherein said one or more polymers are partially crosslinked with the proviso that a strip made of said one or more polymers, obtainable by moulding, meets the above mentioned test.
11. Dental prostheses according to claims 8-10 wherein the polymers forming the prostheses comprise acrylic (co)polymers.
12. Dental prostheses according to claims 8-11 wherein the monomers polymerized for obtaining the polyacrylic resins are alkyl or hydroxyalkyl esters of the acrylic or methacrylic acid, wherein the alkyl group contains from 1 to 8 carbon atoms, or amides and mixtures thereof.
13. Dental prostheses according to claims 8-12 wherein the crosslinking agents are comonomers selected from the following: ethylenglicol di(meth)acrylate, di-, tri-,

tetraethylenglycol di(meth)acrylate, 1,3- 1,4-
butylenglycol di(meth)acrylate, 1,6-hexandiol
di(meth)acrylate, 1,9-nonandiol di(meth)-acrylate, di-
vinylbenzene, trivinylbenzene, allyl (meth)acrylate,
diallyl maleate, diallyl fumarate, triallyl cyanurate,
pentaerythrol triacrylate, trimethylolpropane
tri(meth)acrylate.

14. Dental prostheses according to claims 1-13, wherein the model prosthesis is obtainable by mixing an acrylic (co)polymer in powder form with a liquid acrylic monomer.
15. A process for preparing the dental prostheses according to claims 1-14 comprising the following steps:
 - a) heating a model prosthesis as defined above, at a temperature in the range 105°C-250°C, under atmospheric pressure,
 - b) transferring the prosthesis on a dental plaster cast of a dental arch,
 - c) modelling the prosthesis on the dental plaster cast by adapting it to the shape of the dental plaster cast,
 - d) cooling at room temperature.
16. Use of the dental prostheses according to claims 1-14, to obtain different prostheses, wherein the prostheses of claims 1-13 are subjected to the process of claim 14 by using each time in step c) a different dental plaster cast.

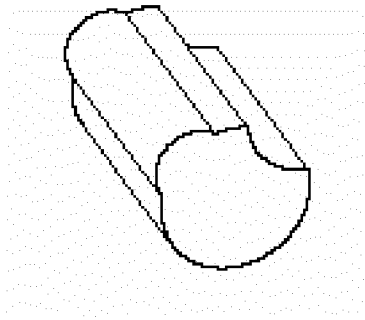


FIG. 1a

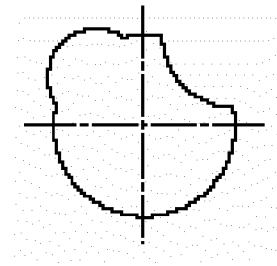


FIG. 1b

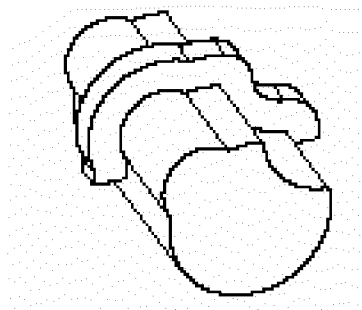


Fig. 2a

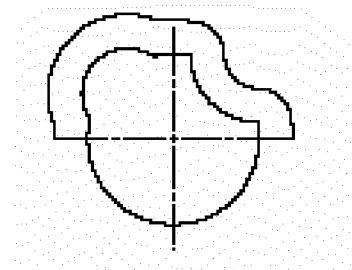


FIG. 2b



Fig. 3



Fig. 4

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/062425

A. CLASSIFICATION OF SUBJECT MATTER
INV. A61C13/107 A61K6/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
A47L A61C A61K

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 practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 016 994 A (SANKIN IND CO) 26 September 1979 (1979-09-26) page 1, line 56 - page 2, line 26 -----	1-12
X	US 2005/042576 A1 (OXMAN JOEL D [US] ET AL) 24 February 2005 (2005-02-24) paragraphs [0017] - [0019], [0021] - [0026], [0031] -----	1-14,16
X	WO 03/015720 A1 (3M INNOVATIVE PROPERTIES CO [US]) 27 February 2003 (2003-02-27) pages 7, 8, 9, page 13 - page 16 page 18 - page 19 pages 23, 32, page 33 ----- -/-	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent 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

"&" document member of the same patent family

Date of the actual completion of the international search

14 August 2014

Date of mailing of the international search report

02/09/2014

Name and mailing address of the ISA/

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Authorized officer

Fouquet, Michèle

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/062425

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/033758 A2 (3M INNOVATIVE PROPERTIES CO [US]; JONES TODD D [US]; KARIM NAIMUL [US]) 20 March 2008 (2008-03-20) pages 3-11 -----	1-14
X	WO 95/35071 A1 (MINNESOTA MINING & MFG [US]) 28 December 1995 (1995-12-28) page 1, lines 14-19 page 8, line 13 - page 17, line 17 -----	1-14,16
X	WO 98/04208 A1 (MIRADENT INTERNATIONAL LTD [US]; GINSBURG STEPHEN J [US]; CAVALIER NEI) 5 February 1998 (1998-02-05) cited in the application claims 1, 4, 5; figures -----	1-11

INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2014/062425

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1-15(partially)
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1-15(partially)

In claim 1, a dental prosthesis, being a device, is claimed. Devices should be defined by their own technical features in order to fulfil the requirements of clarity (Art. 6 PCT). However, in claims 1-6 only a test is defined which the material used to make the dental prosthesis out should fulfil.

In Claim 7, the prosthesis is defined by how it is prepared from (product by process, definition in relation to a second entity, a silicon mould, which is not part of the claimed prosthesis contrary to Art. 6 PCT) without defining the technical features of the dental prosthesis itself. Such a claim lacks clarity (Art. 6 PCT).

In claims 8-14 materials are defined from which the dental prosthesis is formed of. These materials were searched for in relation to the production of dental prosthesis.

In claims 15, 16 a process for preparing a dental prosthesis or a use is claimed, however as in these claims it is referred to unclear claims, these claims are also not clearly defined, especially in view of not clearly defining the material out of which the model prosthesis should be made of.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guidelines C-IV, 7.2), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/062425

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