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(54) Production of ear mouldings and other moulded articles of acrylic polymers

(57) The premature polymerisation of acrylic-polymer-forming materials in the presence of a peroxide catalyst is prevented by the incorporation of a substance reacting with the peroxide to prevent its initiation of the polymerisation, particularly camphorquinone. Polymerisation of the resulting mixture can be initiated by the use of blue light or light including a substantial proportion of blue light. The mixture is particularly valuable for the production of ear mouldings and can be stored for a prolonged period in the absence of blue light.

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SPECIFICATION

Production of ear mouldings and other moulded articles of acrylic polymers

The present invention relates to the production of moulded acrylic polymer articles. It is especially intended for the production of mouldings of the insides of human ears, for example for use with hearing aids, but it can be used for the production of mouldings from other natural mould cavities and from artificial moulds.

Moulded articles are frequently made from acrylic polymers and it is common practice to supply the ingredients for the manufacture of the polymer commercially in two separate packs, and powder and a liquid, the former containing a (partially) polymerised (meth)acrylate ester of a C_1–C_4 alkanol or other acrylic material and the catalyst which is usually a peroxide material and the latter comprising monomeric material, usually a (meth)acrylate ester of such an alkanol. When the powder and liquid are mixed they normally begin to react immediately, provided that the temperature is sufficiently high and the pressure sufficiently great, and reaction continues until the fully hardened state is reached. This reaction can be assisted and the need for high temperatures and pressures avoided by the incorporation of accelerators (for example dimethyl p-toluidine) into the curing mixture in amounts of about 5–10% by weight, but such accelerators are not entirely satisfactory because there is no control over the initiation of the reaction once the ingredients have been mixed, so that there is little or no time to introduce the mixture into a mould cavity such as a human ear after mixing has taken place and before reaction begins. Moreover they tend to discolour the mouldings and the reaction tends to generate heat, which may be undesirable. The unaccelerated compositions are also unsatisfactory for use in making ear mouldings because of the need for heat to initiate curing. The present invention seeks to overcome these disadvantages.

I have found that it is possible to delay the formation of acrylic polymers from a polymerisation reaction mixture containing a peroxide catalyst by the inclusion in the polymerisation reaction mixture of a material which reacts with the peroxide catalyst and which prevents initiation of the polymerisation until blue light or light including a substantial blue component, for example sunlight, is supplied to the polymerisation reaction mixture. Even in the presence of blue light the generation of undesired heat can be avoided because of the absence of an accelerator.

According to the invention a process for producing a moulded article of an acrylic polymer comprises mixing acrylic polymer-forming ingredients, a peroxide catalyst and a substance reacting with the peroxide catalyst to prevent its initiation of the polymerisation, introducing the resulting mixture into a mould cavity and inducing polymerisation by means of blue light or light including a substantial portion of blue light.

The invention also includes a mouldable composition comprising acrylic-polymer-forming materials, a peroxidic catalyst and a quinonoid material in an amount sufficient to prevent initiation of polymerisation of the polymer-forming materials by the peroxidic catalyst except in the presence of blue light or light including a substantial proportion of blue light.

Preformed mixtures of the acrylic polymer-forming materials with the peroxidic catalyst and the peroxide-reacting substance can be produced and supplied, e.g. in sheet or roll form, in a container which is impervious to blue light, for example a bag of darkened polyethylene or other plastics material.

The ingredients used in the formation of the acrylic polymer may be any of the ingredients known or conventionally used for this purpose, especially esters of acrylic and methacrylic acid with low molecular weight alcohols (m. wt.$<$100), and may be the commerically available powder and liquid materials. Where the mould cavity is the human ear or other similar cavity, the ingredients should of course be harmless to the skin. Liquid methyl methacrylate or butyl methacrylate and poly(methyl methacrylate) or poly(ethyl methacrylate) powder are preferred. The ingredients may include inert materials such as fillers, for example silicone powder.

Any convenient peroxidic catalyst can be used. Benzoyl peroxide is frequently used in commercial formulations and can be used satisfactorily for the present invention. It will usually be present in conventional amounts and may be included in the powder component as a result of its production from the corresponding monomer.

The substance which reacts with the peroxide catalyst is preferably a quinonoid material. Some of the simpler quinones such as benzoquinone have an irritant effect on the human system and it is preferred not to use them when the mouldable mixture is to come into contact with humans. I have found that excellent results are achieved by using camphorquinone as the peroxide-reacting substance in the mixture. The amount of peroxide-reacting substance employed is suitably within the range from 0.1 to 2% by weight based on the polymer-forming ingredients, but the optimum figure can be determined by simple experiment. For camphorquinone, the optimum amount has been found to be in the region 0.75% to 1.25%, preferably about 1% (± 0.1) by weight. It is believed that the reaction prevents the peroxide acting as catalyst and causes a delay in polymerisation until free radical polymerisation can be generated by radia-

tion.

The acrylic polymer-forming ingredients may include a monomer containing two arcylic groups and functioning to toughen the finished polymer and to reduce porosity. Esters of unsaturated acids of acrylic type with glycols, particularly of 2 to 4 carbon atoms, more particularly ethylene glycol, are preferred, and a particularly valuable ingredient is ethylene glycol dimethacrylate. Amounts of 5–10% by weight, more preferably about 8%, of this ingredient, or corresponding amounts of other ingredients of this type, serve to increase the toughness of the finished polymer and reduce porosity.

Unexpectedly, I have found that if the amount of this ingredient is increased beyond the proportions mentioned above the mixture is further stabilized in a mouldable form for a considerably extended period. I prefer to use about 15–18% by weight, e.g. 16%, although lesser amounts down to 12% may also be used, if with less effect. When ethylene glycol dimethacrylate, which is a liquid, is incorporated in the mixture in the preferred amounts, as well as the peroxide-reacting substance (e.g. camphorquinone), the mixture can remain in a dough-like, mouldable condition for weeks or even months provided it is kept away from light, for example by being sealed in an air-tight, light-impervious bag or other container. After being removed from the container the mixture can be moulded and then hardened by use of a light pencil as explained.

For carrying out the process of the invention the ingredients forming the polymerisation mixture, the powder and liquid components, may be premixed together with the peroxide-reacting substance and stored out of contact with blue light or light including a substantial proportion of blue light, for example in a tube. Under such conditions the mixture can have an extended shelf-life of 12 months or more. It is of course advisable to avoid exposing the ingredients to high temperatures which may cause premature reaction of the polymer-forming ingredients despite the presence of the peroxide-reacting material. When the formation of the moulding is to be carried out the mixture may be squeezed from the tube into the mould cavity, for example by replacing the cap of the tube with an appropriate nozzle thus forming a syringe, and then activated by blue light or light including a substantial, e.g. predominant, portion of blue light. The use of a thin, directional beam of blue light provides a sensitive control. By blue light I mean light having a wavelength of 4.3 to 4.7×10^{-5} cm.

The process of the invention may be used for making mouldings of various types, but it is particularly valuable for the production of ear mouldings in human ears, for example in the production of hearing aids.

The invention thus includes a process for the production of an ear moulding, comprising mixing acrylic-polymer-forming materials, a peroxide catalyst and from 0.1 to 2% by weight of camphorquinone to form a dermatologically harmless mouldable mixture, filling the resulting mixture into an ear cavity after introduction of an ear stop so as to form a moulding conforming to the inner cavity, subjecting the visible surface of the moulding in situ in the ear cavity to light consisting at least predominantly of blue light to polymerise the surface portion of the moulding, removing the partially polymerised moulding from the ear cavity and completing the polymerisation of the moulding by subjecting it to light consisting at least predominantly of blue light.

If required, it is possible to provide one or more holes in the moulding, for example to accommodate an expanded sponge ear stop for ear mouldings, either by appropriate positioning of tubing in the mould cavity during moulding or in a normal way by drilling the completed moulding.

When applied to the production of ear mouldings the process of the present invention has the great advantage that it is a one-step operation, eliminating the taking of impressions using silicone or other materials and the subsequent dispatch of these impressions to a laboratory for the production of the mouldings.

Further details of the production of ear mouldings are found in my UK Patent No. 2084072 and in UK Patents Nos. 1586432 and 1206852 and such details may be used in the process of the present invention subject to the need to use the composition characterising the invention.

The invention is illustrated in the following Example.

Example

70 parts by weight of a commercially available polyethyl methacrylate powder (containing benzoyl peroxide and 30% by weight of silicone powder as expanding filler) and 100 parts by weight of liquid butyl methacrylate were premixed after incorporation of 1% by weight of camphorquinone into the liquid and the resulting mixture was stored in a tube. After an ear stop had been introduced into the patient's ear, material was squeezed from the tube into the ear until the ear cavity was completely full. Blue light was then directed at the external surface of the mixture in the ear from a light pencil held about 1 cm away and after about 2 minutes this external surface had become hard to a depth of 2 mm and the moulding could be removed from the ear without distortion or damage. After removal, the other surfaces of the moulding were similarly subjected to blue light for a period of about 15 minutes and a fully hardened moulding was obtained. When sawn in half the moulding revealed no porosity.

CLAIMS

1. A process for producing a moulded article of an acrylic polymer comprising mixing acrylic-polymer-forming materials, a peroxide catalyst and a substance reacting with the peroxide catalyst to prevent its initiation of the polymerisation, introducing the resulting mixture into a mould cavity and inducing polymerisation of the polymer-forming materials by means of blue light or light including a substantial proportion of blue light.

2. A process as claimed in claim 1, wherein the substance reacting with the catalyst to prevent its initiation of the polymerisation is a quinonoid material.

3. A process as claimed in claim 2, wherein the quinonoid material is camphorquinone.

4. A process as claimed in any of claims 1 to 3, wherein the proportion of the catalyst-reacting substance is from 0.1 to 2% by weight of the mixture.

5. A process as claimed in claim 3, wherein the proportion of camphorquinone is about 1% by weight of the mixture.

6. A process as claimed in any of claims 1 to 5, wherein the peroxide catalyst is benzoyl peroxide.

7. A process as claimed in any of claims 1 to 6, wherein the polymer-forming ingredients comprise a powder-form partially polymerised C_1–C_4-alkyl (meth)acrylate and a liquid C_1–C_4-alkyl (meth)acrylate.

8. A process as claimed in any of claims 1 to 7, wherein the polymer-forming ingredients include a monomer containing two acrylic groups and present in an amount functioning to toughen the finished polymer and to improve porosity.

9. A process as claimed in claim 8, wherein the mixture includes from 5 to 10% by weight of ethylene glycol dimethacrylate or an equivalent amount of another ester of an unsaturated acid of acrylic type with a glycol of 2 to 4 carbon atoms.

10. A process as claimed in any of claims 1 to 7, wherein the mixture contains from 15 to 18% by weight of ethylene glycol dimethacrylate.

11. A process as claimed in any of claims 1 to 10, wherein the mould cavity is a human ear cavity.

12. A process for the production of an ear moulding, comprising mixing acrylic-polymer-forming materials, a peroxide catalyst and from 0.1 to 2% by weight of camphorquinone to form a dermatologically harmless mouldable mixture, filling the resulting mixture into an ear cavity after introduction of an ear stop so as to form a moulding conforming to the inner cavity, subjecting the visible surface of the moulding in situ in the ear cavity to light consisting at least predominantly of blue light to polymerise the surface portion of the moulding, removing the partially polymerised moulding from the ear cavity and completing the polymerisation of the moulding by subjecting it to light consisting at least predominantly of blue light.

13. A process as claimed in claim 12, wherein one or more holes are formed in the moulding by positioning tubing in the ear cavity during moulding.

14. A process as claimed in claim 12 or 13, wherein the mixture includes about 1% by weight of camphorquinone and 15 to 18% by weight of ethylene glycol dimethacrylate.

15. A process as claimed in any of claims 12 to 14, wherein the mixture includes liquid butyl methacrylate, poly (methyl methacrylate) powder and an inert filler.

16. A process for the production of an ear moulding carried out substantially as hereinbefore described or exemplified.

17. An ear moulding when produced by a process as claimed in any of claims 1 to 16.

18. A mouldable composition comprising acrylic-polymer-forming materials, a peroxidic catalyst and a quinonoid material in an amount sufficient to prevent initiation of polymerisation of the polymer-forming materials by the peroxidic catalyst except in the presence of blue light or light including a substantial proportion of blue light.

19. A composition as claimed in claim 18, wherein the quinonoid material is camphorquinone.

20. A composition as claimed in claim 19, containing about 1% by weight of camphorquinone.

21. A composition as claimed in claim 19 or 20, containing benzoyl peroxide, liquid butyl methacrylate and poly(ethyl methacrylate) powder.

22. A composition as claimed in any of claims 19 to 21, containing 15 to 18% by weight of ethylene glycol dimethacrylate.

23. A composition as claimed in claim 18 and substantially as hereinbefore described.

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