

EUROPEAN QUALIFYING EXAMINATION 1996

**PAPER B
CHEMISTRY**

This paper comprises:

- * Instructions to Candidates
- * Description of the Application
- * Claims
- * Communication
- * Document I (State of the Art)
- * Document II (State of the Art)
- * Document III (State of the Art)
- * Client's Letter

INSTRUCTIONS TO CANDIDATES

In this paper, you should assume that a European patent application for all the Contracting States comprising the appended documents(*) has been filed and that the European Patent Office has issued the annexed official communication. The paper may include a client's letter containing instructions about the way your client wishes to prosecute the European patent application.

You should accept the facts given in the paper and base your answers upon such facts. Whether and to what extent these facts are used is your responsibility.

You should not use any special knowledge you may have of the subject-matter of the invention, but are to assume that the prior art given is in fact exhaustive.

Your task is now to draft a full response to the official communication. The response should be a letter to the EPO, accompanied, if appropriate, by an amended set of claims. No amendments to the description should, however, be made.

The claims should afford the broadest protection possible while meeting the requirements of the Convention. In your letter of response you should set out your arguments in support of the patentability of the independent claim(s).

If you consider that any part of the application ought to be made the subject of one or more divisional applications, you should in a note, clearly identify the subject-matter of the independent claim of such divisional application(s) and the justification for this. However, it is not necessary to draft the wording of the independent claim for the or each divisional application.

In addition to your chosen solution, you may - but this is not mandatory - give, in a note, the reasons for your choice of solution, for example, why you selected a particular form of claim, a particular feature for an independent claim, a particular piece of prior art as starting point or why you rejected or preferred some piece of prior art. Any such note should however be brief.

It is assumed that you have studied the examination paper in the language in which you have given your answer. If this is not so, please indicate on the front page of your answer in which language you have studied the examination paper. This always applies to candidates who - after having filed such a request when enrolling for the examination - give their answer in a language other than German, English or French.

(*) These documents do not necessarily constitute the only or best solution to the task set in Paper A.

DESCRIPTION OF THE APPLICATION

The present invention relates to the development and manufacture of visual aids. Increased importance has been attached recently to visual aids which, for aesthetic as well as partly for medical reasons, are applied directly to the cornea. Such aids are usually referred to as contact lenses.

Various types of contact lenses have already been described, for example in **Document I**, which addresses the important questions in this field and to which reference is made. Express reference is made to the account contained in **Document I** of the development of contact lenses, of the problems related thereto and to the explanation of specialist terms.

Document I relates to glass-clear, strong, cross-linked polymers, obtained by the copolymerisation of (A) a linear or branched polysiloxane macromer and (B) a vinyl and optionally a divinyl monomer, 85 to 100 % of the monomers being water insoluble. These polymers are useful in the preparation of soft or hard contact lenses, particularly hard lenses. The polysiloxane macromer contains at least two terminal or side-chain, polymerisable vinyl groups attached to the polysiloxane by way of a urethane group.

The present invention concerns itself exclusively with polymers for "hard" contact lenses. Increasing prominence has been given to wearing comfort, including the requirement that the wearers encounter no problems when wearing the lenses for lengthy periods. To achieve this wearing comfort, the combination of the following lens properties is necessary: Firstly, a high level of specific oxygen permeability in conjunction with freedom from any allergic reactions or from irritations of the eye should be mentioned. The lenses should also be as scratch-resistant as possible so as to prevent shortening of their service life due to deterioration of optical qualities or wearing comfort. Hard lenses are more fragile than soft ones. Mechanical strength is therefore a particular requirement. Fragile lenses are no longer accepted in the market. Finally, lenses should have a hydrophilic surface (i.e. a good water-wettability) and retain this property throughout their service life. Needless to say, it is essential that the polymer used in their production be glass-clear and streak-free.

The first materials used in the production of contact lenses were polymethyl methacrylate and, later, polymers of substituted alkyl methacrylates such as 2-hydroxyethyl methacrylate (**HEMA**). The latter monomers result, in general, in soft lenses which swell strongly in water.

The incorporation of fluoroalkyl (meth)acrylates and/or silicone macromers into such polymers heralded the breakthrough in achieving higher specific oxygen permeabilities, although this had the disadvantage of reducing lens hydrophilicity. Wearing comfort likewise suffered, as in many cases did the mechanical strength of the lenses. Polysiloxanes which contain polymerisable ethylenically unsaturated groups are also referred to as silicone, siloxane and polysiloxane macromers.

It has been found that the disadvantages of the prior art can be avoided by copolymerising certain siloxane group-containing monomers with certain copolymerisable comonomers in certain quantitative proportions (components (A) to (D) defined below).

Accordingly, the present invention relates to cross-linked, glass-clear, transparent copolymers according to claim 1. The finished polymers contain units of these monomers in practically the same weight proportions as the monomer mixtures themselves. The monomers, being commercially available, are not themselves the subject of this invention.

The invention further relates to a process for the production of these polymers. This process is characterised in that a glass-clear mixture is prepared from the monomers in the stated amount and the initiator, the mixture is degassed by brief exposure to a vacuum prior to polymerisation and the polymerisation is initiated under inert gas.

These polymers are excellently suited to the production of contact lenses. A further aspect of the invention therefore relates to contact lenses made from this material and to a process for their production. This process involves the polymerisation being performed in a mould, the lens blanks thus obtained being machined into the desired shape, and finally the surfaces of the lenses thus obtained being polished.

Component (A) consists mainly or totally of siloxane group-containing monomers, hereinafter referred to as reactive siloxanes (A'). To avoid any misunderstanding, it is pointed out that the term "monomer" as used here is intended to cover all compounds which can be (co)polymerised, i.e. including ethylenically unsaturated oligomers.

The structure of the reactive siloxanes (A') used in accordance with the invention corresponds to formula (1) in **Document I**. It should be noted that separate polymer blocks need not be present in the siloxane either. Whereas the number of siloxane units (= degree of polymerisation) in the silicone macromers used in **Document I** totals between 500 and 1000, the siloxane compounds used in accordance with the invention have a degree of polymerisation of up to 150, preferably 100 to 150. This type of compound with such a limited degree of polymerisation is often described as an oligomer. In the reactive siloxanes (A') of formula (1) which are used here the R groups possess independently of one another the meanings C₁ to C₄ alkyl and/or phenyl. Here it is generally found that the hydrophilicity decreases as the number of C atoms in the R groups increases, i.e. that hydrophobicity already increases significantly when going from C₁ to C₄. The short-chained groups such as methyl and ethyl, and in particular methyl, are therefore preferred. The choice of these groups R also influences the optical properties.

The number of R¹-X- groups in which an ethylenically unsaturated group R¹ is bonded to a silicon atom of the reactive siloxane by a urethane group X is at least 1 in the invention. Their number should not however exceed 25 % of the total number of all the silicon-bonded organic groups (R and R¹-X-). As the examples below show, products with particularly good swelling and mechanical strength characteristics are obtained if these unsaturated groups account for between 5 and 10 % of all these groups R and R¹-X-. For the preparation of these reactive siloxanes reference has only to be made to example 1 and to **Document I**.

These reactive siloxanes are polymerised with comonomers the major proportion of which are methacrylic acid alkyl esters (= alkyl methacrylates) (B). Because of the properties required in the polymer, only the C₁ to C₅ alkyl methacrylates are used. Of these the ethyl, and particularly the methyl ester, are preferred, as the polymers obtained are softer the longer the alkyl group of the methacrylic acid ester and the higher the proportion of these longer-chained alkyl esters.

Also polymerised as further key components are hydroxy group-containing alkyl acrylates and/or methacrylates (C) in order to increase hydrophilicity. Methacrylic ester and acrylic ester of alkane diols, which contain a free hydroxy group are to be mentioned in this connection. Preferably hydroxyethyl or hydroxypropyl methacrylates are used.

The desired high mechanical strength is most easily obtained by using cross-linked polymers. If therefore the reactive siloxanes are not already providing sufficient cross-linkage through several ethylenically unsaturated R¹-X- groups, further polyethylenically unsaturated monomers are also

as such cross-linking agents are compounds having at least two polymerisable ethylenically unsaturated groups, such as neopentylglycol diacrylate or dimethacrylate, to name but a few. Increasing cross-linkage while the leaving the monomer composition otherwise unchanged makes the polymer harder and reduces its swelling capacity.

To obtain polymers that meet the necessary requirements the monomers are copolymerised in the following proportions: component (A) in amounts of 15 to 40 % by weight, the alkyl methacrylates (B) in amounts of 40 to 80 % by weight, the hydroxy group-containing (meth)acrylates (C) in amounts of 2 to 10 % by weight and the cross-linking agents (D) in amounts of up to 10 % by weight. Of crucial importance for the polymer thus obtained is that the degree of cross-linking is such that the polymer does not swell in water by more than 10 vol.%, so as to ensure that the polymer, and the contact lens obtained from it, has sufficient dimensional stability. On the other hand, the Shore-D hardness should not exceed 85. This figure is a simple indication of the limit value for the required mechanical strength.

In component (A), a part of the reactive siloxanes (A') can be replaced by fluoroalkyl methacrylates (A'') of which the fluoroalkyl groups contain 2 to 10 C atoms. The amount of these fluorinated monomers should not exceed 10 % by weight of the total amount of the components (A) to (D). The longer the fluoroalkyl group, and the higher the total amount of this fluorinated monomer (A'') and of the reactive siloxane (A'), the less hydrophilic is the polymer. Under no circumstances, therefore, should the total amount of this component (A), i.e. (A')+(A''), exceed 40 % by weight, as hydrophilicity will otherwise fall below an acceptable limit value. This limit value is defined by the contact angle (see **Document I**) which must be at least 100°.

The monomers are admixed in the above proportions and 0.001 to 0.5 % by weight of initiator (E) is added. No other substances, e.g. solvents, are added to the mixture. The monomer mixture must already be glass-clear and streak-free. Numerous tests have shown that monomer mixtures that are not streak-free always produce polymers which are unsuitable for the intended purpose because of their unsatisfactory optical properties.

To prevent bubbles of entrapped gas being formed in the mixture, this is briefly placed in a vacuum prior to starting the polymerisation. After degassing, polymerisation under inert gas is then started either thermally (using peroxide group-containing radical-forming initiators) or photochemically (by means of photo-initiators). The polymers can be regarded as being identical, irrespective of the method used for initiating the reaction. The degree of polymerisation of the polymers is kept in the required range by using the stated amount of initiator and ensuring that the reaction temperature does not rise beyond 60° C.

Usually polymerisation for the production of contact lenses is performed in a mould with a space approximately the same shape as the lens, so that lens blanks are produced directly. This ensures good reaction heat dissipation and further reduces the likelihood of the formation of streaks. To reduce this still further, polymerisation is preferably started photochemically. This obviates the need for external heat and it prevents the reaction mixture overheating.

Furthermore, this method of polymerisation in the mould simplifies subsequent processing and avoids excessive material loss. The blanks are then machined to achieve their exact shape, following which the surfaces are polished. The more dimensionally stable the polymer is, the simpler these stages in processing are. These stages are common knowledge among skilled practitioners.

The following examples are intended to explain the invention in greater detail. Reference is made

Example 1

As described in **Document I**, a reactive siloxane with three polymerisable methacrylate groups bonded to siloxane groups was made from a dimethyl siloxane oligomer having a degree of polymerisation of 100 which contained three hydroxyethyl groups per molecule, diisocyanate and hydroxyethyl methacrylate (**HEMA**).

Examples 2-7

The reactive siloxane produced in example 1 was copolymerised with the monomers listed in table 1 into 0.1 mm thick films following addition of 0.2 % by weight of a UV photo-initiator commercially available as "UVInit A" by irradiation with UV light between plates of quartz glass which have been treated so as to be non-sticking. Measurements of the specific oxygen permeability (O_2 -DK) were carried out on these films. Using the same method, 1 mm thick sheets were made from each monomer mixture and used to determine their water wettability.

In a similar way, and as described in **Document I**, samples for hardness measurements were also made and examined.

Water swelling was determined by measuring the increase in volume of samples after standing for 48 hours in distilled water at 20° C. The samples were produced by the method described for the hardness measurement. The value for Shore-D hardness should never be less than 70. Below this limit the polymers are too soft. The results are summarised in table 1.

Examples 8-10

In a manner analogous to example 1, a reactive siloxane was produced which had a degree of polymerisation of 100 and contained polymerisable methacrylate groups, their number being 10% of all the organic groups bonded to siloxane groups. This reactive siloxane was used to repeat examples 2, 3 and 4. The results are shown in table 1.

Tests with various commercially available photo-initiators or monomer-soluble peroxide group-containing radical-forming initiators consistently produced polymers with negligibly small amounts of residual monomers.

Incidentally these polymers can also be used for other applications for which good transparency and water wettability are essential, such as for containers or for optical lenses.

Table 1

Ex.	Comonomers (wt.%, balance to 100%: reactive siloxane)	Appearance	O ₂ -DK	Contact angle	Shore-D hardness	Swelling (Vol. %)
2	MMA (60) HEMA (4)	clear	34	110°	73	6.9
3	MMA (66) HEMA (4)	clear	28	117°	75	7.4
4	MMA (73) HEMA (4)	clear	17	123°	80	8.7
5*	MMA (87) HEMA (4)	clear	7.5	124°	83	9.5
6	MMA (60) NPDA (4) HEMA (4)	clear	25	117°	77	5.9
7	MMA (60) FPMA (4) HEMA (4)	clear	33	101°	70	7.5
8	MMA (60) HEMA (4)	clear	34	110°	79	5.2
9	MMA (66) HEMA (4)	clear	28	118°	81	5.6
10	MMA (73) HEMA (4)	clear	16	123°	83	5.9

MMA = methyl methacrylate

FPMA = hexafluoroisopropyl methacrylate

* Comparison test

HEMA = 2-hydroxyethyl methacrylate

NPDA = neopentylglycol diacrylate

"clear" means glass-clear in each case

CLAIMS

1. Cross-linked, glassclear, transparent copolymers with a degree of cross-linking which prevents the polymers from swelling in water by more than 10 % by volume, and with a Shore-D hardness not exceeding 85, obtainable by copolymerisation of glass-clear, streak-free monomer mixtures containing an initiator (E) in an amount of 0.001 to 0.5 % by weight of the monomers, said monomer mixtures consisting of
 - (A) 15 to 40 % by weight of a component which is (A') a siloxane of the formula (1), $R_3Si-O-[(R^1-X)Si(R)-O]_m-[Si(R)_2-O]_n-SiR_3$ (1), wherein the number of siloxane units does not exceed 150, R = independently of one another C₁- to C₄-alkyl or phenyl, and at least one R¹-X- group with the meaning given in the description is present, and wherein the number of R¹-X- groups does not exceed 25 % of the total number of all silicon-bonded organic groups; wherein (A') may be partly replaced by (A'') which is a fluoroalkyl methacrylate in which the fluoroalkyl group contains 2 to 10 C atoms, in an amount of no more than 10 % by weight of the total weight of the components (A) to (D),
 - (B) 40 to 80 % by weight of a methacrylic acid alkyl ester the alkyl group of which contains 1 to 5 C atoms,
 - (C) 2 to 10 % by weight of an hydroxy group-containing acrylate and/or methacrylate, and
 - (D) 0 to 10 % by weight of compounds having at least two ethylenically unsaturated copolymerisable groups.
2. Process for the production of polymers according to claim 1, characterised in that a glassclear mixture is prepared from the monomers in the stated amounts with the initiator, the mixture is degassed by being placed briefly in a vacuum prior to polymerisation, and the polymerisation is subsequently initiated under inert gas.
3. Use of the polymers of claim 1 for the manufacture of contact lenses.
4. Contact lens made from a polymer according to claim 1.
5. Process for the production of the contact lens according to claim 4 using the process according to claim 2, characterised in that the polymerisation is performed in a mould, the lens blank thus obtained is shaped into the desired form by machining and the surfaces of the lens thus obtained are finally polished.

COMMUNICATION

1. Before comment is given on patentability it should be noted that the claims do not meet the requirements of Art. 84. Thus in claim 1, contrary to Rule 29(6) EPC, the R^1-X group is not defined.

According to the description the lower limit of the Shore-D hardness of the polymers is 70, that of the contact angle 100° , and the claimed production process may not exceed a reaction temperature of 60° C. This information should also appear in the claims.

2. **Document II** discloses clear, transparent polymers obtained from the same monomers as in the present application. The amounts of the monomers used would also appear to be the same (cf. the example in the document). This also applies to the initiators used in the homogeneous monomer mixtures. According to page 5 and the penultimate paragraph of the description, the polymers are to be viewed as identical, irrespective of the initiator used, so that restricting the claim to a photochemical initiation described as being preferred cannot be viewed as being suitable for the purpose of delimitation. The document also recommends degassing the reaction mixture prior to polymerisation. Claims 1 and 2 therefore lack novelty with respect to **Document II** (Art. 52(1) and 54(1) and (2) EPC).
3. Likewise, the monomer mixture in **Document III** corresponds to the definition in claim 1. This is especially true for the reactive siloxane in **Document III**, which conforms to the definition of formula (1) of claim 1 ($m = 1$) (see the Guidelines for Examination C-IV, 7.4).
4. Furthermore, **Document III** makes a clear reference to the use of the resultant polymers for contact lenses. The document also recommends polymerisation in a mould and further processing of the lens blank in the same way as described in claim 5.
5. **Document III** therefore clearly anticipates the subject-matter of claims 3 to 5 (Art. 52(1) and 54(1) and (2) EPC).
6. **Document III** also points to the possibility of varying the properties of the polymers and contact lenses as desired by selecting the components used and their amounts. This should be borne in mind in any argumentation, provided that novelty of the claims can be established. In so doing account should also be taken of the disclosure of **Document I**, in which exactly the same photo-initiator is used to produce the polymer for contact lenses.
7. You are invited to submit claims which take the aforementioned objections into account and which comply with the requirements of the EPC, especially with regard to novelty, inventive step, clarity, disclosure in the documents as filed and unity (Arts. 54(1) and (2), 56, 84, 123(2) and 82 EPC).

In your reply you should also identify the difference between the new claims and the state of the art and its significance, and present the invention in such a way that both the technical problem to be solved vis-à-vis the state of the art and the solution found (see Rule 27(1)(c) EPC), and your position on the matter of inventive step can be understood.

According to the Guidelines (C-III, 4.4) an independent claim should specify clearly all

indicate all the features which are necessary to solve the problem on which the application is based.

8. Attention is drawn to the fact that the application may not be amended in such a way that its subject-matter extends beyond the content of the application as filed (Art. 123(2) EPC). Therefore, and also in view of Guidelines E-II, 1 and C-VI, 5.4, it should be explained from where in the original application documents new features in newly formulated claims have been directly and unambiguously derived.

DOCUMENT I (State of the Art)

(This document is identical to Document I in Paper A)

The present invention relates to glass-clear, strong, cross-linked polymers, obtained by the copolymerisation of (A) a linear or branched polysiloxane macromer containing at least two terminal or side-chain polymerisable vinyl groups attached to the polysiloxane by way of a urethane group and (B) a vinyl and optionally a divinyl monomer, 85 to 100 % of the monomers being water-insoluble. These polymers, which must of course be streak-free, are useful in the preparation of soft or hard contact lenses, particularly hard lenses.

Contact lenses fall into two main categories, normally called "hard" and "soft", but which are better distinguished by the mode in which they are fitted to the eye. Hard lenses are rather loosely fitted to facilitate tear-liquid exchange between lens and cornea. This they do by their "rocking-chair" motion, by which they continuously pump tear liquid out from the space between lens and eye surface. Such tear-liquid exchange is the only way by which the extremely important oxygen is supplied to the cornea of the wearers of conventional hard contact lenses made from polymethyl methacrylate (PMMA). Hard PMMA lenses are, at least initially, uncomfortable and irritating for the wearer because the blinking eyelid hits a hard edge. They are nevertheless popular because they can be made with great precision by machining (or lathing) and polishing. This is especially important for the production of lenses of asymmetrical design for the correction of astigmatism. Another advantage of hard lenses is that they are very easy to keep clean.

Soft contact lenses on the other hand adhere closely to the cornea and are therefore much more comfortable for the wearer. Since they allow only limited tear liquid exchange they have to possess a specific oxygen permeability high enough to prevent damage to the eye even if they are worn only for a period of hours. In all commercially available soft lenses (made, for example, from hydrophilic hydroxyethyl methacrylate) this O_2 permeability is a function of their water content. In addition, water acts as a plasticiser, which gives the lens its softness and the necessary hydrophilicity which allows it to swim on the cornea rather than to stick to it. Sticking to the cornea is the main problem with hydrophobic soft lenses, such as the known silicone-rubber lenses. Although soft hydrophilic lenses offer higher comfort, optical precision is open to question since precise shaping is not possible because of the softness of the material and because certain distortions due to water swelling are unavoidable. Because they tend to adjust to the cornea, soft lenses are not suitable for the correction of astigmatism. Added to this is the inconvenience of lens-care procedures with standard soft lenses.

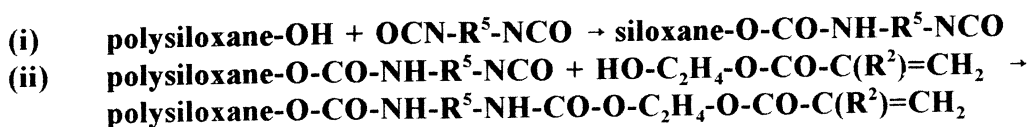
The object of an embodiment of this invention is to provide a silicone-containing lens the surface of which is permanently hydrophilic. It is a further embodiment of this invention to provide silicone-containing polymeric materials which range from "soft" to "hard" (using contact-lens terminology) but which do not exhibit the above-described drawbacks.

The polysiloxane macromer corresponds to the general formula (1), wherein the $-(R^1-X)Si(R)-O-$ and $-[Si(R)_2-O]-$ groups need not be in the form of separate polymer blocks, but may, for example, be spread more-or-less statistically, e.g. evenly, throughout the molecule:



wherein R = methyl, ethyl, propyl or butyl, R^1 = an ethylenically unsaturated group, in particular $CH_2=C(R^2)-CO-O-$, $R^2 = H$ or CH_3 , $X = -R^3-O-CO-NH-R^5-NH-CO-O-R^4-$, each of R^3 and R^4 = a linear or branched (divalent) alkylene residue and R^5 a linear or cyclic alkylene residue, and $m \geq 2$, $n > 0$ and $500 \leq (m + n) \leq 1000$.

The siloxane macromers are obtained in a two-step reaction from free hydroxy group-containing polysiloxane, diisocyanate and e.g. hydroxyethyl (meth)acrylate as follows:



Styrenes or C_1 - to C_{12} -alkyl, C_6 - to C_{12} -cycloalkyl or C_6 - to C_{12} -aralkyl acrylates or methacrylates can be used as comonomers. The longer-chained esters are better suited for soft lenses. Small amounts of divinyl compounds or hydroxyalkyl, as well as C_2 - to C_{10} -fluoroalkyl acrylates and/or methacrylates, such as hydroxyethyl methacrylate and hexafluoroisopropyl methacrylate, can also be used.

The polymers obtained were tested as follows.

Specific oxygen permeability (O_2 -DK) was determined by measuring the permeability for dissolved oxygen at 35° C using a polarographic electrode in an air-saturated aqueous environment and is expressed in "Barrer" units: $10^{-11} \text{ ml cm}/(\text{cm}^2 \text{ s mmHg}) (=7.50 \cdot 10^{-14} \text{ ml cm}/(\text{cm}^2 \text{ s Pa}))$. Below a value of 15 the specific O_2 permeability is hardly viewed as satisfactory.

Water wettability was determined by immersing at 36° C a 1 mm thick sample sheet in water saturated with n-octane. An n-octane droplet was allowed to rise to the lower surface of the sheet and the **contact angle** of the droplet was measured. In this measurement high numbers signify high wettability (hydrophilicity).

Hardness was determined using a **Shore-D** durometer on polished surfaces of a button cut from the centre of a polymer blank (cf. DIN 53 505, ASTM D-2240, ISO 868).

It is of course common knowledge that quantitative figures for polymers and oligomers only represent average properties according to a statistical Gauss distribution.

Example 1

A reactor fitted with a stirrer was filled under inert gas with 30 mols of polydimethyl siloxane which contained three hydroxyethyl groups and which had a degree of polymerisation of 500. 94.5 mols of hexane diisocyanate (a commercial alkylene diisocyanate) were then added together with 25g dibutyltin dilaurate as catalyst. After stirring for 5 hours at 50° C the conversion was practically complete.

25 mols of this intermediate product were reacted with 76 mols of hydroxyethyl methacrylate (**HEMA**) under inert gas at room temperature until no more isocyanate groups (**-NCO**) were present. The resulting product consisting of polysiloxane having methacrylate groups had a purity of more than 99.5 %. This product is referred to below as siloxane macromer.

Examples 2-4

The siloxane macromer prepared according to example 1 was copolymerised with the monomers listed in table 1 into 0.1 mm thick films, following the addition of 0.2 wt.% "UVInit" initiator, by irradiation with UV-light between quartz glass plates which had been treated so as to be non-sticky. These films were used to measure specific oxygen permeability. In the same manner 1 mm thick sheets made from each monomer mixture were used for determining water wettability.

In the same manner, buttons of 15 mm diameter and 10 mm height were polymerized in cylindrical polypropylene moulds. The cylindrical buttons were then cut in half and the flat surfaces polished for the measurement of hardness.

The results are summarised in the following table 1:

Ex.	Comonomers (wt. %, balance to 100 %: siloxane macromer)	Appearance	O ₂ -DK	Contact angle	Shore-D hardness
2	MMA (64) HEMA (4)	clear	29	96°	68
3	CHMA (66) HEMA (4)	clear	28	94°	66
4	MMA (60) FPMA (4) HEMA (4)	clear	32	100°	64
5	MMA (50) NPDA (16) HEMA (4)	clear	28	90°	68
6	CHMA (50) NPDA (16) HEMA (4)	clear	27.5	88°	67
7	MMA (72) HEMA (4)	clear	17	98°	76
8	MMA (86) HEMA (4)	clear	7.8	103°	80

MMA = methyl methacrylate

HEMA = 2-hydroxyethyl methacrylate

CHMA = cyclohexyl methacrylate

NPDA = neopentylglycol diacrylate

FPMA = hexafluoroisopropyl methacrylate

"clear" means glass-clear in each case

case

DOCUMENT II (State of the Art)

The expert in the field of packaging of liquids constantly faces the problem of a lack of breaking strength of the containers. Various attempts have therefore already been made to overcome this problem.

Acrylic polymers, which are visually very attractive, have been used since the early days as a high-quality packaging material. However, the breaking strength has not sufficed for all requirements. This is the reason why for some time attempts have been made to improve this property by modifying the polymers.

This objective is achieved by the polymeric packaging material according to the invention which, because of its degree of cross-linking and hardness, has a very high breaking strength. Like the known types of acrylate used as packaging material mentioned above, the packaging material in accordance with the invention is also visually very attractive and hence offers a further advantage for use in show-room displays.

The invention relates to containers for liquids, such as bottles and flasks made from cross-linked, glassclear, transparent copolymers with degrees of cross-linking which prevent water swelling of the polymers of more than 5 vol. %, and with a Shore-D hardness of between 70 and 85. The polymers are obtained from the copolymerisation of a homogeneous monomer mixture. The mixture consists of

- (a) 40 to 80 % by weight of alkyl methacrylate the alkyl groups of which possess 1 to 5 C atoms,
- (b) 2 to 10 % by weight of hydroxyalkyl methacrylates and
- (c) 15 to 40 % by weight silicones of the formula

$$\mathbf{R_3Si-O-[(R^1-X)Si(R)-O]_m-[Si(R)_2-O]_n-SiR_3} \quad (1)$$

In formula (1) $1 \leq m \leq 3$, $(m + n) \leq 150$, R = independently of one another C_1 - to C_4 -alkyl, $R^1 = CH_2=C(R^2)-CO-O-$, $R^2 = H$ or CH_3 , $X = -R^3-O-CO-NH-R^5-NH-CO-O-R^4-$, R^3 and $R^4 = -(CH_2)_t-$, $t = 2$ to 4 , $R^5 = -(CH_2)_v-$, $v = 2 - 6$. Preferably $m = 1$.

In addition, the monomer mixture contains a monomer-soluble initiator in an amount of 0.001 to 0.5 % by weight of the monomers. The initiator is preferably a monomer-soluble peroxide group-containing radical-forming compound. The glassclear monomer mixture can be polymerised as such or in solution. As the polymerisation is inhibited by oxygen it is important that no air be present. This is most readily achieved by exposing the initiator-charged monomer mixture to a vacuum several times prior to polymerisation and then flushing it with a dry inert gas such as nitrogen. By this, formation of gas bubbles in the polymer is prevented, as well.

In order to improve the properties of the products according to the invention, and in particular their resistance to damage from dropping, a cross-linking agent is preferably added, immediately before further processing, to the polymers to cross-link the hydroxy groups of the polymer when the containers are produced, by injection moulding, for example. The amount of cross-linking agent is preferably kept slightly below the stoichiometric amount. The remaining free hydroxy groups enable the surface to retain a certain hydrophilicity, thus enabling aqueous liquids, in particular, to flow off easily. This prevents the formation of unsightly droplets.

Short-chained alkylene diisocyanates are particularly suitable as cross-linking agents. The preferred cross-linking agent is hexane diisocyanate (**HDI**). Care should be taken to ensure that

linking agents.

Example

A siloxane oligomer of dimethyl siloxane units with a degree of polymerisation of 100 which contained three polymerisable methacrylate groups (R^1-X) in the molecule was prepared from the corresponding siloxane having three hydroxyethyl groups with **HDI** and hydroxyethyl methacrylate (**HEMA**).

A monomer mixture was then made up from 60 parts by weight methyl methacrylate, 36 parts by weight of the above-attained siloxane component, 4 parts by weight **HEMA** and 0.03 parts by weight benzoyl peroxide and polymerised in a moisture- and air-free environment at 55° C. Two parts by weight of **HDI** were then incorporated in the polymer which was then shaped into bottles by injection moulding, during which the polymer cross-linked. The breaking strength of these bottles was significantly greater than that of bottles not cross-linked with **HDI** but otherwise produced in the same way. In breaking tests the cross-linked semi-filled bottle samples consistently achieved drop heights of between approx. 120 and 130 cm, in contrast to non-cross-linked samples, where the figure lay between approx. 90 and 100 cm.

The cross-linked bottles were visually attractive and exhibited good wettability with aqueous solutions, so that the bottles were drop- and streak-free when emptied, and the content flowed out smoothly.

These advantages were also found with bottles made from the same monomer components with a weight proportion of 70:25:5.

DOCUMENT III (State of the Art)

The object of the invention is novel contact lenses made from glass-clear, transparent, streak-free copolymers, obtainable by polymerisation of a mixture containing 0.001 to 0.5 % by weight of initiator, based on the monomer content, said mixture consisting of

- (a) 45 to 60% by weight of alkyl methacrylate,
- (b) 4 to 10% by weight of hydroxyalkyl acrylate and/or methacrylate,
- (c) 25 to 40% by weight of a silicone of the formula (1)

$$\text{R}_3\text{Si-O}-(\text{R}^1\text{-X})\text{Si}(\text{R})\text{-O}-(\text{Si}(\text{R})_2\text{-O})_n\text{-SiR}_3,$$
 wherein **R** independently of one another is C₁- to C₅-alkyl, **R**¹ = CH₂=C(**R**²)-CO-O-, with the proviso that the **-[(R¹-X)Si(R)-O]-** unit may be located at any point on the polysiloxane chain, 100 ≤ **n** ≤ 150, **R**² = H or CH₃, **X** = -**R**³-O-CO-NH-**R**⁵-NH-CO-O-**R**⁴, **R**³ and **R**⁴ independently = a linear or branched alkylene group, and **R**⁵ = a divalent butane, pentane and/or hexane group,
- (d) 1 - 10 % by weight compounds with at least two ethylenically unsaturated copolymerisable groups.

The contact lenses according to the invention can be made to be from soft to hard depending on the methacrylic acid alkyl esters chosen. The shorter the alkyl residue, the harder the lens. Therefore, for the preferred soft contact lenses long-chained methacrylates, such as butyl, octyl or dodecyl methacrylate, are used. For less preferred harder to hard lenses in particular, methyl methacrylate is used.

Lens hydrophilicity can be controlled by the mixing proportion of components (b) and (c). Whilst (c) reduces lens hydrophilicity, the hydroxy group present in (b) increases this property, as well as increasing water absorption. This has the further effect of improving specific oxygen permeability and thus complements the effect of component (c). The components (c) and (d) also increase the toughness or the breaking strength of the lenses. Shore-D hardness can be set at between 50 and 80, for example by the selection of (a) and the amount of the crosslinking agent (d). By increasing the amount of (d) the degree of cross-linking can be increased sufficiently to lower water swelling of the polymers to below 10 % by volume.

In this way, the properties of the contact lenses according to the invention can be adjusted to almost any desired extent.

The polymerisation is preferably carried out in a mould with a lens-shaped space, and after removal from the mould the blanks thus obtained can be machined (lathed), the surfaces polished, to obtain the required optically precise lens form. Soft lenses are then stored in water.

A contact lens made of 55 % by weight n-butyl methacrylate, 8 % by weight hydroxyethyl acrylate, 32 % by weight silicone of the formula (1) with **R** = **R**² = CH₃, **R**³ = **R**⁴ = C₂H₄, **R**⁵ = (CH₂)₆ and with **n** = 100, the polymerisable group being incorporated approximately in the centre of the siloxane chain, and 5 % by weight neopentylglycol dimethacrylate, exhibited following properties: **Shore-D hardness** (ISO 868): 57, **O₂-DK** (according to **Document I**): 30, **swelling** (after 48 hours in distilled water at 20° C): 21 vol. %. After the swelling treatment the lens was covered with a continuous film of water.

CLIENT'S LETTER

Dear Sir/Madam,

Thank you for forwarding us the communication from the Patent Office. Unfortunately, the examiner appears not to understand the invention correctly and to have raised objections which have absolutely nothing to do with our products.

While the polymers in **Document II** are similar to ours, they only relate to packaging material. In our view **Document III** is likewise completely irrelevant. The document describes a contact lens that is clearly soft and exhibits strong swelling.

Nor does either of these two document contain any reference at all to the presence of fluoroalkyl methacrylate in the lens material.

With regard to a further aspect please find below a number of further tests showing the importance of phenyl groups in component (A'), a fact not to be found in any of the documents. The significance of these groups is that their presence makes it possible to control the refractive index. Higher refractive indices of course make savings in lens thickness possible. Please consider whether these results can be submitted to the examiner in order to convince him of our invention. Examples 2 and 8 have both been repeated, in each case a part of the methyl groups in the reactive siloxane has been replaced by phenyl. The higher refractive indices can be seen in the table. We have also listed wettability, although it is lower. The refractive indices n_D^{25} in examples 2 and 8 were 1.485 and 1.490 respectively.

Compared with example	2		8	
	1:15	1:2.5	1:15	1:2.5
Phenyl/methyl ratio	1:15	1:2.5	1:15	1:2.5
Refractive index	1.498	1.505	1.500	1.511
Contact angle	104°	102°	102°	100°

Yours faithfully

Perspicacious plc