N-ALKYL-N-(METH)ACRYLOYLOXYALKYLCARBOXAMIDES OF AROMATIC CARBOXYLIC ACIDS AND AROMATIC CARBOXYLIC ACID ANHYDRIDES, AND ADHESIVES CONTAINING THESE COMPOUNDS

The invention relates to new N-alkyl-N-(meth)acryloyloxyalkylcarboxamides of aromatic carboxylic acids and aromatic carboxylic acid anhydrides, their preparation and formulations of these compounds for use as adhesives for the treatment of dental hard substance.

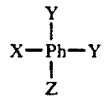
A particularly serious problem of conservative dentistry is permanent glueing, without gaps at the edge, of filling materials made of plastic to the dental hard substance (dentine and dental enamel). Polymeric materials which harden are used as filling materials for dental repairs in the dental sector. Acrylate-based fillings, which shrink during hardening and thus contribute to the formation of gaps at the edges, are preferred as the polymeric materials which harden.

These polymeric fillings furthermore have the disadvantage that they remain poorly stuck to the dentine. To solve this problem, undercuts in the dentine have sometimes been made; for this it has been necessary to remove considerable amounts of fresh dentine, beyond the region affected. According to another method, the dentine and the enamel surface are etched superficially with acids, such as, for example, phosphoric acid, and the filling is then undertaken. Apart from the fact that the acid has an irritating effect in the oral region, it also easily penetrates through the dental canaliculi into the tooth and damages the nerve (pulp). Substance mixtures of 4-methacryloyloxyethyl trimellitate (4-MET) or the 4-methacryloyloxyethyl ester of trimellitic anhydride (4-META) with ethylenically unsaturated monomers and free radical initiators are described as adhesion promoters for fillings in the dental sector in U.S. Pat. No. 4,148,988. A commercial product based on 4-META (Superbond from Sun Medical) has to be mixed with methyl methacrylate (MMA), polymethyl methacrylate (PMMA) and partly oxidised tri-n-butylborane (TBB) to obtain the form ready for application (MMA-4-META-TBB resin/Y.-S. Kuo, Proc. Natl. Sci., Counc ROC (B) Volume 8, No. 2 (1984), 187–192). Mixtures of 4-META. of similarly complicated build-up and with the addition of a polyfunctional (meth)acrylate are also described (EP 266 220). Corresponding mixtures containing isomeric methacryloyloxyethyl esters of naphthalenetricarboxylic anhydride (4-MENTA) are also known (I. Harashima et al., Dental Materials Journal 7, 2 (1988) 141–150). Although DOS (German Published Specification) 3,510,962 states that a chloroform solution of 4-MENTA can also be used without further additives, an additional operating step is then necessary for subsequent application of MMA, PMMA and TBB. None of these adhesion promoters is capable of producing fillings free from gaps at the edges; an optimised photochemically initiated adhesive based on 4-META also gave gaps at the edges both in the enamel and in the dentine region of a filling made of plastic (K. Nagata et al., Journal of Biomedical Materials Research 18 (1984) 1089–1103). The fact that the enamel and dentine regions of one and the same cavity must be treated with different etching or cleaning solutions has been pointed out elsewhere as a further hindrance to the use of the 4-META-containing Superbond (Dirass Report E 9 - 4, Biocompatible Materials for the Oral Cavity, Dia Research Institute Inc., 1987).

A monomer related to 4-META. for use in dental adhesion promoters was reported with pyromellitic acid di-2-methacryloyloxyethyl ester (PMDM) (R. L. Bowen et al., J. Dent. Res. 61, 9 (1982) 1070–1076), this also being employed in a commercial product (Tenure from Den Mat). The use of this product is also described as complicated in the above literature reference, since the dentine must be treated with a surface-active comonomer in an additional operating step before application of the adhesion promoter. This product has also been incapable of ensuring fillings free from gaps at the edges.

It has now been found that adhesives for the treatment of dental hard substance which allow glueings which are free from gaps at the edges, coupled with a simple composition and easy handling, can be formulated with the aid of the new N-alkyl-N-(meth)acryloyloxyalkylcarboxamides of aromatic carboxylic acids and aromatic carboxylic acid anhydrides (I).

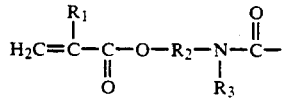
The new compounds correspond to the formula (I)



(I)

in which

X represents an N-alkyl-N-(meth)acryloyloxyalkylcarboxamide of the formula



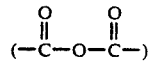
wherein

R_1 denotes hydrogen or methyl,

R_2 denotes a divalent aliphatic radical (C_2–C_6) and

R_3 denotes a monovalent aliphatic radical (C_1–C_4),

Y represents COOH, it also being possible for adjacent groups Y to be linked to form an anhydride group



Z represents H, X or, if Y denotes COOH, Y and

Ph represents a tri- or tetrasubstituted benzene ring (1,2,3-/1,2,4- or 1,2,4,5-substitution) or a tri- or tetrasubstituted naphthalene ring (1,2,6-/1,4,5-/2,3,6-/1,4,5,8- or 2,3,6,7-substitution).

(Meth)acryloyl derivatives in the context of the present compound ar derivatives of acrylic acid and of methacrylic acid.

The various substituents and alkyl and aryl radicals of the N-alkyl-N-(meth)acryloyloxyalkylcarboxamides according to the invention in the context of the general formula (I) in general have the following meaning:

A divalent aliphatic C_2–C_6- radical (R_2) in general denotes a divalent straight-chain or branched hydrocarbon radical having 2 to 6, preferably 2 or 3, carbon atoms. The following divalent aliphatic radicals may be mentioned as examples: butanediyl, dimethylethanediyl, pentanediyl, neopentanediyl, hexanediyl, 2,3-dimethylbutanediyl, methylethanediyl, propanediyl and ethaned-