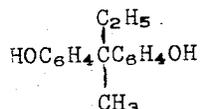


The bismethacrylates containing about 50% or more of the ester in which $m + m'$ is 2 tend to contain more or less crystals of that bismethacrylate, the higher esters are not crystalline and, in fact, can dissolve appreciable amounts of the crystalline materials. These esters are all suitable in dental filling compositions.

EXAMPLE 5

Another approach to the elimination of crystallinity is by use of bisphenol B



in place of bisphenol A. The reactions of Example 1 are repeated using the proportional amount of bisphenol B and ethylene oxide in 10 mole % excess and the hydroxyethylated bisphenol B is converted to the bismethacrylate which is a honey-colored oil which resists all efforts at inducing crystallization. Viscosity is 3,770 cps. It is suitable in restorative compositions.

EXAMPLE 6

The procedure of Example 1 is modified to use sodium methoxide as catalyst instead of triethylamine and propylene oxide is condensed with bisphenol A. The reaction is less exothermic and slower but proceeds readily. Conversion to the bismethacrylate gives a yellow oil with Brookfield viscosity of 3,200 cps. which is suitable in restorative compositions.

EXAMPLE 7

This example provides comparisons between the binders of this invention which are free from active hydrogen atoms and prior art binders which contain active hydrogen atoms as hydrophilic OH groups.

Several dental restorative compositions are made for comparison of compressive strengths. The compositions are designated as A, B, C and D. Each is filled using a fine crushed glass material, treated with vinyl silane as described in Chang U.S. Pat. No. 3,452,437 and additionally including a coating of about 0.7% of benzoyl peroxide. The binder is thus milled with the filler and catalyst at the same time.

Restorative A is prepared from 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) and glycidyl methacrylate essentially as described in the above Bowen and Chang patents using 90.4 parts glycidyl methacrylate 66 parts bisphenol A and about 0.78 parts dimethyl-p-toluidine. A small amount (about 0.025 parts) of hydroquinone monomethyl ether is present to inhibit polymerization during reaction. About 1.76 parts of triphenylborane ammonia are added as described in the Chang patent together with a further 0.83 parts of dimethyl-p-toluidine. As a reactive diluent, 17.8 parts of methyl methacrylate are added to the product as suggested by both Bowen and Chang. Ground glass filler prepared as described above is included to 72%, i.e., 28 parts binder and 72 parts filler.

Restorative B includes a hydroxyethylated biphenol A bis methacrylate binder of the invention prepared as described in Example 1 but using sodium methoxide as catalyst and incorporates the same filler in the same amount as in Restorative A.

Restorative C also includes a hydroxyethylated bisphenol A bismethacrylate as in Restorative B but from

a different batch as binder and 65% of the same filler as in Restoratives A and B.

Restorative D is like Restorative C and uses the same binder to which is added 15% of triethylene glycol bismethacrylate as a reactive diluent. The combined binder is then filled using 70% of the same filler as used in the other restoratives.

Cylindrical test samples, about 6 mm. in diameter and 12 mm. high with parallel surfaces, are prepared using suitable amounts of each binder together with the standard catalyst-filler combination described above. Mixing time is fairly short, about 1 1/4 minutes and the samples are then hardened in the mold in an oven at 37° C.

Testing for compressive strength is in an Instron Tester using 0.05 cm./min. rate for application of compression and is followed noting the rate of distortion so that the yield point, referred to as proportional limit, at which increase of distortion with increasing load starts to deviate from being essentially linear.

Some test specimens are stored in water at 37° C. and tested by the same procedure after various periods of time.

The compressive strengths and yield points (both in pounds per square inch) are tabulated in Tables 2 and 3 respectively both initially (either dry or after 24 hours wet storage) and after prolonged wet storage.

TABLE 2

Restorative	Compressive Strength		Prolonged Wet Storage	
	Dry Strength	Wet Strength (24 hrs. stor.)	Strength	Time
A	27,000	—	21,600	5 mos.
B	28,000	—	29,200	4.5 mos.
C	—	27,800	28,500	57 days
D	—	30,500	29,900	57 days

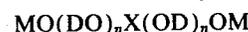
TABLE 3

Restorative	Yield Point		Prolonged Wet Storage	
	Dry Strength	Wet Strength (24 hrs. stor.)	Strength	Time
A	22,000	—	10,200	5 mos.
B	17,000	—	15,600	4.5 mos.
C	—	15,500	18,200	57 days
D	—	17,500	18,100	57 days

It will be evident that the composition including the prior art binder decreased significantly on wet storage in compressive strength and even more in the yield point whereas restoratives of the invention were not significantly affected by wet storage. This will be an evident advantage of the instant restoratives.

What is claimed is:

1. A stable dental restorative composition having, after hardening and exposure to moisture, moisture absorption of less than 1 percent by weight, said composition comprising glassy or crystalline inorganic non-metallic filler and, as binder, a liquid polymerizable organic binder consisting essentially of 0.05 to 5 percent of mononuclear aromatic tertiary amine accelerator for free-radical polymerization and a polycarbinol polymethacrylate or polyacrylate, substantially free from active hydrogen atoms and devoid of peroxides, of the formula



wherein M is methacrylate or acrylate, D is unsubstituted alkylene of 2 to about 6 carbon atoms, n is 1 to 4