

criteria are met. Typical of such polymeric materials are poly (methyl methacrylates), polycarbonates and the like. Of these, polycarbonates are preferred due to their better dimensional stability during environmental changes. In some instances, glass, quartz or other transparent inorganic materials may be used as the substrate. Typically, polymeric materials are preferred due to their low cost and the ease of manufacturing discs therefrom.

Blank disc substrates may be formed by conventional molding methods, such as injection molding or injection/compression molding methods, or they may be cut or stamped from preformed sheets of the substrate material. In one embodiment of this invention the geometry of the substrate is formed before lamination of the photohardenable layer. In an alternative embodiment, the geometry of the substrate is cut or stamped from sheets of substrate material after the photohardenable layer has been laminated thereto. In the alternative embodiment, it is possible to carry out all the manufacturing steps before cutting or stamping the disc from the processed sheet laminate.

#### B. Dry Photohardenable Film

As used herein, the term "dry photohardenable film" or "dry photohardenable layer" refers to a substantially solvent-free polymeric layer having a creep viscosity of about 20 megapoises or greater and preferably between about 100 and 200 megapoises, as measured with a parallel plate rheometer. Such "dry photohardenable layers" are contrasted with conventional liquid photohardenable layers which typically have viscosities of about several hundred poises or less. For the purpose of this invention, viscosity is measured as creep viscosity with a parallel plate rheometer using a Du Pont Model 1090 Thermal Mechanical Analyzer. In this procedure, a 0.036 inch thick sample is placed in contact between two flat discs (about 0.25 inch diameter). A quartz probe which is capable of accepting additional weights is positioned atop the upper disc and the same/disc assembly is maintained at constant temperature of 40° C. and RH of 44% throughout the measurement. Creep viscosity is calculated from the rate of decrease of sample thickness under equilibrated conditions. The 0.036 inch sample is prepared by laminating together sufficient layers of the test film to obtain the desired thickness. The laminate is then cut to provide a circular sample slightly larger in diameter than that of the rheometer plates.

The photohardenable layer is laminated to the substrate as a preformed dry film photohardenable element comprised of a temporary support sheet or web and a uniformly thick dry photohardenable layer releasably adhered thereto. The photohardenable element may be cut sheets or it may be in the form of a rolled web for ease of use and storage. The non-laminated second side of the photohardenable layer may have a removable protective cover film which is removed before use by stripping it off.

Uniformly thick, dry, photohardenable layers useful in this invention typically have a thickness which complements the thickness of the substrate so that the thickness criteria of the finished product is met.

The photohardened layer should be firmly adhered to the substrate surface and should have optical characteristics comparable to those of the surface. Preferably the refractive index of the photohardened layer should match that of the substrate  $10 \pm 0.1$  measured at the end use radiation.

The photohardenable layer is a thermoplastic composition which upon exposure to actinic radiation, polymers of higher molecular weight by crosslinking and/or by polymerization. This changes the rheological character of the composition and decreases its solubility in common solvents. Preferred photohardenable compositions are photopolymerizable compositions wherein free radical addition of polymerization and crosslinking of a compound containing one or more ethylenically unsaturated groups, hardens and insolubilizes the composition. The photosensitivity of the photopolymerizable composition is enhanced by a photoinitiating system which may contain a component which sensitizes the composition to practical radiation sources, e.g., visible light. Conventionally a binder is the most significant component of a substantially dry photopolymerizable film or layer in terms of what physical properties the film or laminate will have while being used in the process of the invention. The binder serves as a containing medium for the monomer and photoinitiator prior to exposure, and after exposure contributes to the optical and other physical characteristics needed for the optical element. Cohesion, adhesion, flexibility, miscibility, tensile strength, and index of refraction (IR) are some of the many properties which determine if a binder is suitable for use in an optical element. In practicing the invention dry film photopolymerizable elements of various types may be used such as those disclosed in U.S. Pat. No. 3,469,982; U.S. Pat. No. 4,273,857; U.S. Pat. No. 4,278,752; U.S. Pat. No. 4,293,635; U.S. Pat. No. 4,621,043; U.S. Pat. No. 4,693,959; U.S. Pat. No. 3,649,268; U.S. Pat. No. 4,191,572; U.S. Pat. No. 4,247,619; U.S. Pat. No. 4,326,010; U.S. Pat. No. 4,356,253 and European Patent Application 87106145.3 filed Apr. 28, 1997. All of these are incorporated herein by reference.

Other equivalent dry film photohardenable film elements include photodimerizable or photocrosslinkable compositions such as disclosed in U.S. Pat. No. 3,526,504 or those compositions in which hardening is achieved by a mechanism other than the free radical-initiation identified above.

In general the photopolymerizable compositions useful in carrying out this invention contain an ethylenically unsaturated monomer, a free radical-generating initiating system and a binder.

Suitable monomers which can be used as the sole monomer or in combination with others include the following: t-butyl acrylate, 1,5-pentanediol diacrylate, N,N-diethylaminoethyl acrylate, ethylene glycol diacrylate, 1,4-butanediol diacrylate, diethylene glycol diacrylate, hexamethylene glycol diacrylate, 1,3-propanediol diacrylate, decamethylene glycol diacrylate, decamethylene glycol dimethacrylate, 1,4-cyclohexenediol diacrylate, 2,2-dimethylolpropane diacrylate, glycerol diacrylate, tripropylene glycol diacrylate, glycerol triacrylate, trimethylolpropane triacrylate, pentaerythritol triacrylate, polyoxyethylated trimethylolpropane triacrylate and trimethacrylate and similar compounds as disclosed in U.S. Pat. No. 3,380,831, 2,2-di(p-hydroxyphenyl)-propane diacrylate, pentaerythritol tetraacrylate, 2,2-di(p-hydroxyphenyl)-propane dimethacrylate, triethylene glycol diacrylate, polyoxyethyl-2,2-di(p-hydroxyphenyl)-propane dimethacrylate, di-(3-methacryloxy-2-hydroxypropyl) ether of bisphenol-A, di-(2-methacryloxyethyl) ether of bisphenol-A, di(3-acryloxy-2-hydroxypropyl) ether of bisphenol-A, di(2-acryloxyethyl) ether of bisphenol-A,