

Light-Induced Cure of Epoxy Resins. Use of a Manganese Carbonyl as Photosensitizer

Epoxy resins are generally cured by the addition of nucleophiles rather than by use of free-radical sources. Most light-sensitive compounds therefore will not serve as photosensitizers for cure of epoxy resins. The few known light sensitizers^{1,2} for these resins are either thermally unstable or are not available commercially. The dimensional stability, mechanical strength, and chemical resistance of epoxy resins have therefore been unavailable for application in the imaging sciences. We have found that certain transition metal carbonyls will serve as photosensitizers for the cure of several types of commercial epoxy resins.³

The following example illustrates the use of methylocyclopentadienyl manganese tricarbonyl as a photosensitizer: A tinplate panel at 150° is covered with a 2-mil coating of a mixture containing 81.5% EPON resin 1004 (Shell Chemical Company, Polymers Division), 16.0% Nadic methyl anhydride (Allied Chemical Company, Industrial Chemicals Division), and 2.5% methylocyclopentadienyl manganese tricarbonyl (Ethyl Corporation, Petroleum Chemicals Division, Combustion Improver CI-2). The plate is covered with a stencil, mask, or photographic negative and is irradiated for 15 min at room temperature with light from a General Electric AH-6 high-pressure mercury arc 30 cm distant. The plate is then baked in a well-ventilated oven at 125°C for 2 hr. After 15 min of baking, carbon monoxide bubbles rise in the exposed film, but at 125°C they collapse before the film gels. After 2 hr in the 125°C oven, the plate is cooled, soaked in methyl ethyl ketone, and rubbed with steel wool to develop the image. Cured areas are unaffected by the methyl ethyl ketone or steel wool treatments. The developed plate may be returned to the oven and baked at 150°C an additional 2 hr to complete the



Fig. 1. Cotton cloth decorated with epoxy resin formulation described in text. Formulation applied in tetrahydrofuran solution, allowed to dry overnight, covered with stencil, exposed to AH-6 lamp for 15 min, baked 2.5 hr at 125°C, soaked in methyl ethyl ketone to remove unexposed resin. Letters in image are 1.9 cm in height.

cure. It may then be used as a stamping tool or may be inked with a brayer and used as a printing plate. The shrinkage accompanying cure is negligible; the image of the stencil is faithfully reproduced in resin (Fig. 1). In addition to metals, other materials such as wood, cloth, glass, or plastic will also serve as substrates for the photosensitive resin. Mineral fillers, Eponol resin, nylon, PVC, metal powders, and leveling agents commonly used as additives in epoxy resin formulations may also be included in the recipe. Dye, such as du Pont Oil Blue A, may be added during the development step. In the dark, the resin mixture has a "pot life" of several weeks.

In order to provide a resin which will cure at room temperature or below, a trimercaptan curing agent may be substituted for the anhydride used in the example above. Polymercaptan-containing coatings can be formulated so as to dry to the touch in less than 10 hr at room temperature after exposure to light yet have pot lives of several weeks.

Direct sunlight, sunlamps, 365-millimicron "black light" lamps, 254-millimicron low-pressure mercury lamps, or ^{60}Co gamma radiation are also effective, but exposures of several hours are required. A 1-kilowatt General Electric AH-6 lamp or an 8-kilowatt PAX pulsed xenon lamp is a convenient source of light having suitable intensity and wavelength. According to Lynch,⁴ the action spectrum for decarbonylation extends to 550 nm; ultraviolet wavelengths therefore appear unnecessary.

It is believed that the manganese carbonyl functions as a photosensitizer because it is oxidized under irradiation to a manganese(II) salt which is a catalyst for the nucleophilic addition of anhydride or mercaptan curing agent to epoxy units. Manganese(II) salts are effective catalysts for such additions in the dark. Air is not an inhibitor of the curing reaction.

CAUTION: Methylcyclopentadienyl manganese tricarbonyl vapor is extremely toxic.

References

1. J. J. Licari and P. C. Crepeau, U.S. Pat. 3,205,157 (September 7, 1965).
2. W. R. Workman, U.S. Pat. 3,074,869 (December 23, 1960).
3. W. S. Anderson, patents pending.
4. M. A. Lynch, Brit. Pat. 843,088 (August 4, 1960); *C. A.*, **55**, 6848 (1961).

W. S. ANDERSON

Shell Development Company
P.O. Box 24225
Oakland, California 94623

Received April 23, 1971