

# Barrier Coats Versus Inert Atmospheres. The Elimination of Oxygen Inhibition in Free-Radical Polymerizations

D. A. BOLON and K. K. WEBB, *Chemical Synthesis & Processes Branch, Chemical Laboratory, Corporate Research & Development Center, General Electric Company, Schenectady, New York 12301*

## Synopsis

The polymerization of UV-curable coatings that react by a free-radical mechanism is subject to oxygen inhibition which can be avoided by utilizing an inert atmosphere. We demonstrate that wax barrier coats used to prevent evaporation of volatile reactive monomers are equally effective in preventing oxygen inhibition. No quantitative difference is found between the degree and rate of polymerization in an inert atmosphere or with a wax barrier coating. However, when used above a given ceiling temperature, the wax barrier allows oxygen diffusion which inhibits cure.

## INTRODUCTION

Free-radical polymerizations are widely used to effect the cure of thin films of solventless (100% solids) coatings. Such polymerizations may be initiated by the thermal decomposition of peroxides, electron beams, or exposure to ultraviolet light. Problems arise where atmospheric oxygen inhibits cure of solventless coatings by reacting with the initiator radicals or the polymer radicals.<sup>1</sup> In the case of thin-film coatings, air inhibition results in substantial amounts of unpolymerized monomer as well in a nonpolymerized, tacky surface in the coating itself. Consequently, the films fail to develop their expected physical properties.

Substantial volatilization of monomer from thin films will result in a surface rich in the less volatile components such as the prepolymers. In styrene-polyester resins, this will ultimately result in a tacky surface similar to the one resulting from oxygen inhibition. Early work<sup>2-5</sup> demonstrated that surface tack caused by monomer evaporation in styrene-containing polyester resins can be eliminated by suitable additives such as paraffin wax. Schroeter and Moore<sup>6</sup> showed that the addition of small amounts of wax eliminates surface tack when styrene polyesters are cured by ultraviolet light.

Acrylic coatings containing relatively volatile monomers are subject to the same problems; i.e., the monomers evaporate easily and the polymerization shows marked oxygen inhibition. Since certain acrylic coatings often contain even higher concentrations of monomer than polyesters, evaporation is an even greater problem. Schroeter et al. have shown that evaporation control can also be obtained in acrylic formulations by wax additives.<sup>7</sup>

It appeared important to examine the effect of a wax barrier on the oxygen inhibition during polymerization of acrylic coatings in thin films and to compare it to the uninhibited polymerization in an inert atmosphere. For certain applications, it was significant to explore whether an inert atmosphere over wax-

containing acrylic coatings might increase either the rate or the degree of polymerization.

## RESULTS AND DISCUSSION

### Acrylic Resins

#### *Oxygen Inhibition*

Formulations used for these studies consisted of saturated acrylic polymers dissolved in acrylic monomers. These formulations were sensitized to permit polymerization by free-radical initiation upon exposure to UV light. When required, the resins contained small amounts of paraffin wax for monomer evaporation control.<sup>7</sup> While not examined in this work, polymerizations initiated by other methods such as electron beam or redox reactions are expected to show similar behavior.

To determine the degree of polymerization, samples of films were exposed for a given length of time to UV light, and the unpolymerized monomer was then baked out by heating the samples for 3 hr at 150°C. Figure 1 shows a plot of the residual monomer in films drawn on glass slides as a function of exposure time.

The polymerization is slow at first because of the large amount of monomer and the relatively low viscosity of the resins. The autoacceleration that occurs after several minutes of UV exposure is caused by the rapid viscosity increase in the acrylic coating as the monomer polymerizes, known as the gel effect, or the Tromsdorff effect.<sup>8</sup> In the end, as the monomer is depleted, polymerization slows to a diffusion-controlled rate until rigidity of the system prevents further polymerization leaving less than 5% unreacted monomer in the film.

On polycarbonate substrates, the initial slow polymerization is eliminated (Fig. 2). The reaction proceeds directly with the autoacceleration phase until monomer depletion slows the polymerization. The cure in air at 43°C in Figure 2 is a normal "uninhibited" cure due to the presence of an efficient wax barrier.

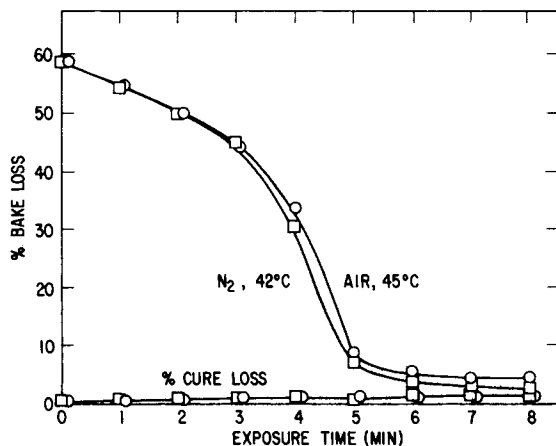


Fig. 1. UV cure of 2-mil films of resin [60 parts by weight methyl methacrylate and 40 parts acrylic polymer with 1% 135°F (57°C) wax] on glass in air or nitrogen atmosphere.

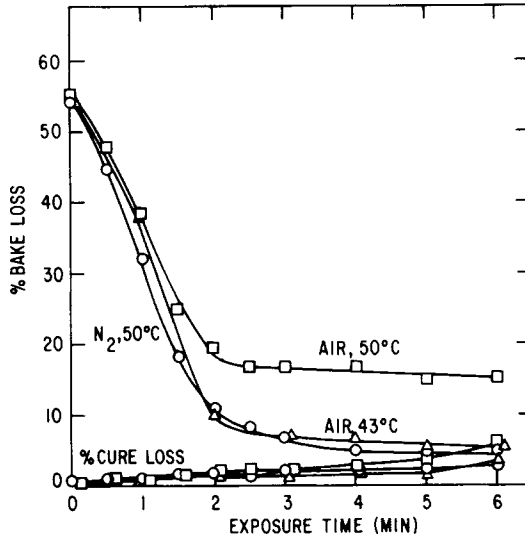


Fig. 2. Effect of temperature or nitrogen atmosphere on the UV cure of 2-mil films of resin (60 parts by weight methyl methacrylate and 40 parts polymer with 1% 135°F (57°C) wax) on polycarbonate substrate.

In some cases the rapid polymerization abruptly stops leaving much more than 5% residual monomer. Figures 2 (in air, 50°C) and 3 (in air, 50°C) show the inhibited polymerization occurring after 2 min where continuing the UV exposure for 8 min does not further polymerize the monomer. We explain this abrupt termination of polymerization by a failure of the wax barrier coat to control oxygen inhibition (as well as monomer volatilization). The barrier coat fails because the temperature of the substrate and of the coating finally exceed a limiting temperature determined by the particular wax. It is possible to increase this ceiling temperature by replacing the wax additive with one of a higher melting point. For example, if the failing 135°F (57°C) wax used in the formulations shown in Figures 2 and 3 is replaced by a 145°F (62°C) wax, complete control of oxygen inhibition is obtained under similar cure conditions (Fig. 4).

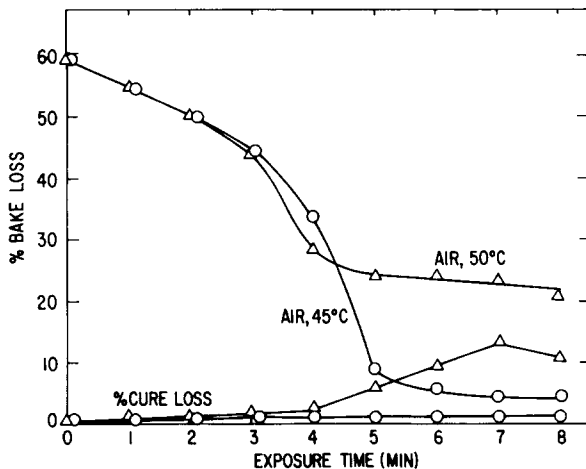


Fig. 3. Effect of temperature on UV cure of 2-mil films of resin [60 parts by weight methyl methacrylate and 40 parts acrylic polymer with 1% 135°F (57°C) wax] on glass in air.

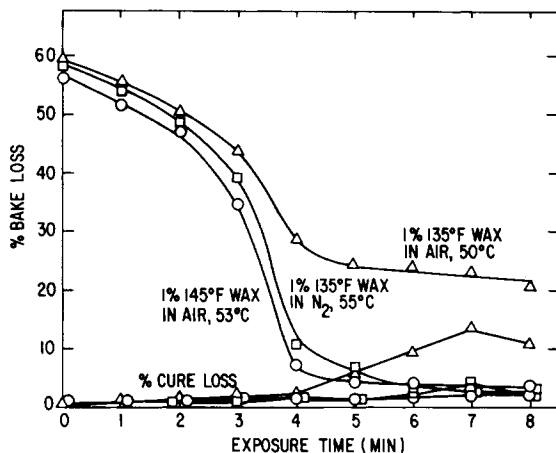


Fig. 4. Effect of melting point of 1% wax additive on UV cure of 2-mil films of resin (60 parts by weight methyl methacrylate and 40 parts acrylic polymer) on glass in air or nitrogen atmosphere.

When a nitrogen atmosphere is used over the acrylic resin containing a properly working wax barrier, there is *no* difference in rate (Fig. 1). However, a nitrogen atmosphere used over an acrylic system containing a failing, low-melting wax (see, in air, 50°C data in Figs. 2 and 4) eliminates oxygen inhibition, and normal, uninterrupted curve results. In addition to the increased monomer conversion in nitrogen, the evaporation loss of monomer is reduced, probably due to the more rapid rate of polymerization.

We conclude that wax can be an effective oxygen barrier and can prevent oxygen inhibition of free radical polymerization as effectively as an inert atmosphere. A combination of wax and an inert atmosphere does not appear to offer improvement.

#### *Evaporation Control*

Acrylic monomers such as methyl methacrylate have a high volatility. In cases where their rates of polymerization are relatively slow (i.e., where polymerization requires several minutes), it is necessary to prevent evaporation during cure. This can be accomplished by use of a paraffin wax additive.<sup>7</sup> All our figures show, in addition to the amount of unreacted monomer, the amount of monomer lost by evaporation during UV exposure. Figure 1, for example, in the upper set of data, shows the decreasing amount of unreacted monomer (bake loss) with increasing UV exposure. The second, lower set of data shows the increasing loss due to evaporation during polymerization.

The data show the extremely good control of monomer evaporation by a properly working wax additive—virtually no monomer evaporation. When the cure temperature is allowed to rise as shown in Figure 3, a significant increase in monomer evaporation occurs after several minutes of exposure to UV light. Since the samples are cold at the start and heat up upon exposure to the hot mercury vapor lamps, the sharp upward turn in the evaporation rate probably signals that the film has reached a temperature where the wax film begins to fail. It should be noted that failure of control of monomer evaporation and oxygen inhibition occurs simultaneously.

As discussed by Schroeter et al.,<sup>7</sup> the wax barrier coat for evaporation of monomer dissolves in the resin at some characteristic temperature and no longer provides a barrier to evaporation. It is possible to raise this limit by substituting the wax with one of a higher melting point as shown in Figure 4. Such a new wax will also raise the temperature at which oxygen inhibition begins to occur.

### Other Resin Systems

Because of the high volatility of the acrylic monomers examined in the first section, it was not possible to examine polymerization in an inert atmosphere without using wax to control evaporation. Less volatile acrylics such as isobornyl methacrylate could be substituted for methyl methacrylate in the resins because these monomers are poor solvents for the polymer. It was found, however, that a resin/monomer mixture could be prepared from an unsaturated polyester prepolymer and a monomer with low volatility. The monomers isobornyl methacrylate and *p-tert*-butylstyrene are sufficiently nonvolatile so that polymerizations can be carried out with wax free systems without significant monomer losses. We examined for comparison a system consisting of a polyester prepolymer with styrene monomer which require a wax additive.

**Isobornyl Methacrylate.** An unsaturated polyester formulated with isobornyl methacrylate was polymerized with and without wax in air as well as in an inert atmosphere. The polymerization (followed by baking out unpolymerized monomer) proceeds at a faster rate than in the all acrylic system due to the increased concentration of polymer (70% compared to only 40% in the acrylic system) as well as the presence of vinyl unsaturation in the polymer. Figure 5 shows that there is no rate difference between a UV-initiated polymerization with a wax barrier versus one without wax in an inert atmosphere. However, when both the wax and the inert atmosphere are omitted, significant oxygen inhibition occurs. The polyester-isobornyl methacrylate system was also examined to determine the minimum concentration of wax needed for control of

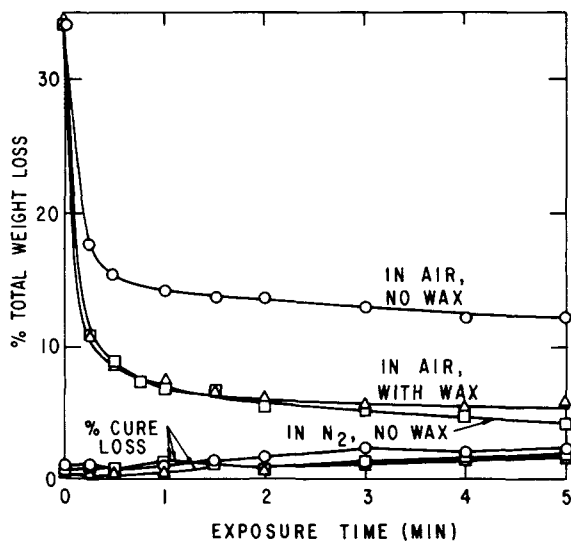


Fig. 5. Effect of addition of 1% 135°F (57°C) wax or nitrogen atmosphere on UV cure of 2-mil films of resin (30 parts by weight isobornyl methacrylate and 70 parts of polyester resin) on glass.

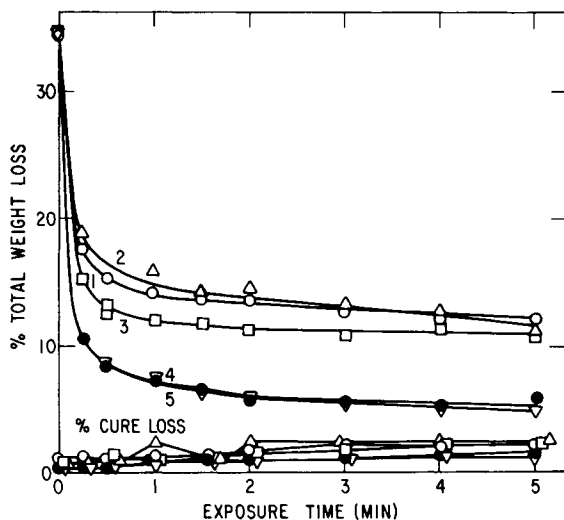


Fig. 6. Effect of 135°F (57°C) wax concentration on oxygen inhibition of cure of 2-mil films of resin (30 parts by weight isobornyl methacrylate and 70 parts polyester resin) on glass in air: (○) (1) 0% wax; (△) (2) 0.1; (□) (3) 0.2; (▽) (4) 0.3; (●) (5) 1.0.

oxygen inhibition. Figure 6 shows that 0.3% wax gives complete control, while increases in concentration up to 1% wax did not provide further improvement.

**Styrene and *p*-tert-Butylstyrene.** When a resin is formulated with an unsaturated polyester and styrene, wax must be present for evaporation control.<sup>6</sup> As in the case of the acrylic formulations, this system shows no difference in cure whether an inert atmosphere is present or not (Fig. 7). It is possible to eliminate the wax and conduct cures without significant monomer loss by replacing the styrene with the less volatile *p*-tert-butylstyrene. In this system, as in the isobornyl methacrylate system, oxygen inhibits cure of the resin unless the air is replaced by an inert atmosphere (Fig. 8). In this system wax, if present, prevents oxygen inhibition and allows polymerization similar to the inert atmosphere.

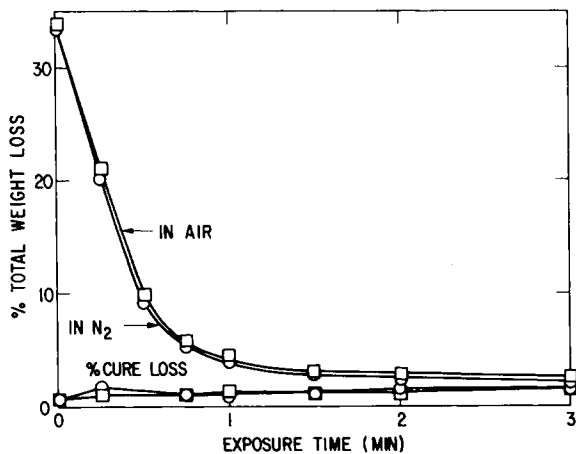


Fig. 7. Effect of air or nitrogen atmosphere on UV cure of 2-mil films of resin [70 parts by weight styrene and 30 parts polyester resin with 0.2 parts 135°F (57°C) wax] on glass.

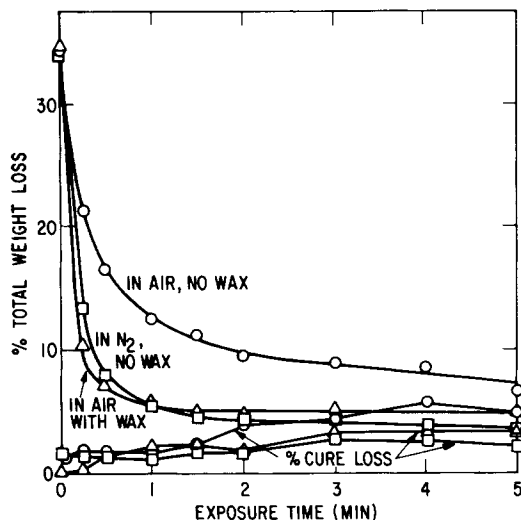


Fig. 8. Effect of addition of 0.2 parts 135°F (57°C) wax or nitrogen atmosphere on UV cure of 2-mil films of resin (70 parts by weight of *p*-*tert*-butylstyrene and 30 parts polyester resin) on glass.

## CONCLUSIONS

In the UV-initiated vinyl polymerization of resins applied as thin films, oxygen inhibition limits monomer conversion. As much as 50% of the monomer in films may remain unpolymerized after lengthy UV exposure.

Wax, added to prevent monomer evaporation, prevents oxygen inhibition. Replacement of oxygen by an inert atmosphere over a properly formulated wax-containing resin does not further reduce inhibition or accelerate polymerization. There exists a specific upper temperature limit for each wax. When this limit is exceeded, both evaporation and oxygen inhibition occur. This temperature limit can be raised by selecting a wax with a higher melting point.

## EXPERIMENTAL

### Resins

**Polyacrylates.** These resins consist of methyl methacrylate monomer (60 pbw), an acrylic resin, Elvacite 2013 (E. I. du Pont de Nemours Co.) (40 pbw), benzoin ethyl ether (2 pbw), and the indicated amount of wax (135°F wax, 1 pbw).

**Polyesters.** A polyester resin which contains fumarate esters (70 pbw) is combined with the appropriate monomer (styrene, *p*-*tert*-butylstyrene, or isobornyl methacrylate, 30 pbw), benzoin ethyl ether (2 pbw), and paraffin wax (135°F wax, up to 1 pbw) to give the desired resin.

### Substrates

The substrates for the cure studies were either 2 in. × 3 in. glass microscope slides or 3 in. × 3 in. plaques of polycarbonate sheet 120 mils thick.

### UV-Cure Light System

The cure system consisted of four medium-pressure mercury arc lamps (General Electric H1000A-36-15) in aluminum reflectors, ballasted with General Electric 9T64Y 118G5 ballasts and arranged in a rectangular array to deliver a wide, even flux of light over approximately 2 square feet. To reduce the heat delivered to the substrate, we used a filter system composed of two rolled Pyrex (Corning Glass Co.) glass sheets cooled with circulating air. This system substantially reduced the heat while reducing the light only 20%.

It was possible to obtain some heat control during polymerization on glass substrates by use of a heat sink, i.e., a cooled metal block. However, the low thermal conductivity of polymers prevent use of this method with substrates such as polycarbonate so that the above filters had to be used.

The whole UV cure system was operated in a fume hood to help remove heat as well as volatile emissions from polymerizing films.

### UV Cure Chamber

When a controlled atmosphere was desired, the cure system included a closed metal box fitted with a quartz window. The inert gas, nitrogen, was admitted to one end of the box while slits in the other end allowed the gas to exit.

When the system was operating properly, it was possible to purge all residual oxygen (to <0.3%) with a nitrogen flow of 45 SCFH. The oxygen concentration was measured in the box with a Fieldlab (Beckman Instrument Co.) monitor which showed 0.1–0.3% oxygen at the point of uninhibited cure.

### UV Cure

The degree of cure of a resin was determined by measuring the residual un-polymerized monomer that could be baked out of exposed films. By weighing a panel before and after coating applications, after cure, and after a 1-hr bake at 150°C (3-hr bake for polycarbonate), it was possible to determine a loss during cure (“cure loss”), a loss during bake (“bake loss”), and the total weight loss (“cure and bake loss”) of the coating.

To obtain reproducible data, it was necessary to standardize time increments such as purging the gas chamber 1 min after sample insertion to allow oxygen equilibration and allowing overnight equilibration of the polycarbonate samples after baking to achieve reproducible weights.

### Temperature

An iron–Constantan thermocouple was placed on the surface of the film to be cured and the surface temperature recorded on a Leeds and Northrup AZAR recorder during exposure.

### Resin Application

A doctor blade with a 4-mil gap was used to spread the resin on the substrate. The applied wet film thickness was typically one half the blade gap, in this case 2 mils, which leaves a thin enough coating to observe surface effects but contains enough material for weighing ease.



**References**

1. C. Walling, *Free Radicals in Solution*, Wiley, New York, 1957, p. 169.
2. T. L. Phillips, *Brit. Plast.*, 69 (1961).
3. K. Demmler, *FATIPEC Congress*, 8, 237 (1966).
4. W. Trimborn, *FATIPEC Congress*, 4, 149 (1957).
5. W. Gebhardt, W. Herrmann, and K. Hamann, *Farbe und Lack*, 64, 303 (1958).
6. S. H. Schroeter and J. E. Moore, in *Nonpolluting Coatings and Coating Processes*, J. L. Gardon and J. W. Prane, Eds., Plenum Publishing, New York, 1973, p. 135.
7. S. H. Schroeter, D. A. Bolon, K. K. Webb, and J. E. Moore, 2nd International Meeting on Radiation Processing, Oct. 22-26, 1978, Miami, Florida.
8. E. Tromsdorff, H. Köhle, and P. Lagally, *Makromol. Chem.*, 1, 169 (1948).

Received May 23, 1977

Revised June 8, 1977