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The award consists of $1,000, expenses covering attendance at the FSCT Annual Meeting and International Coatings Expo to receive the award, and a suitably inscribed plaque for the best paper submitted during the award year.

The award was established in 1986, by the Southern Society for Coatings Technology as sponsors, in memory of an honored Past-President of the Society, Alfred L. Hendry.

Curing Profiles of the New Xenon Chloride Lamp

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The cure rate of a high gloss overprint varnish was compared using a standard medium pressure mercury lamp and a high intensity xenon chloride lamp. Samples with equal photoinitiator concentration cured at a much faster rate using the xenon chloride lamp. It was found that the concentration of the photoinitiator could be greatly reduced and still give rapid rates of curing when the xenon chloride lamp with peak output at 308 nm was used.

INTRODUCTION

Developments in the field of UV curable coatings have exploded over the past 15 years. One innovation is new lamps being developed to cure the coatings. After a review of selected background information on the UV curing of coatings, this paper will present results which compare curing trials of a new xenon chloride lamp from Fusion Systems Corporation to the traditional medium pressure mercury lamp.

Radiation curing has become a significant part of the coatings industry. Photocuring is fairly cheap, effective, and durable.[1] There are two primary methods in which the coating can be photocured (the forming of chemical bonds which in turn form a web crosslinking the coating's mixture to make the coating hard). Electron beam curing effects crosslinking by using ionizing radiation to create free radicals; the other method uses ultraviolet radiation which creates free radicals through the breakdown of a photoinitiator. This paper will focus on UV curing.

The speed at which a coatings mixture can be cured (curing time) depends on the amount of UV radiation penetrating the surface.[2] The more light of the appropriate wavelength reaching the photoinitiator molecules the greater the number of free radicals that will be generated. The UV light is generated by special lamps; however, the sun and fluorescent lights give off UV radiation but not of sufficient intensity for practical application.

In a UV-curable coatings mixture, there are usually three main ingredients: photoinitiator, prepolymer, and diluent. The photoinitiator is a chemical which when exposed to UV radiation of wavelengths between 200-400 nm[3] breaks down to form free radicals.[1] These free radicals react with the diluent's or the prepolymer's double bonds to form a chain propagating species. Polymerization then ensues, and crosslinking can occur if the chain has more than one double bond present. A simplified example is depicted in *Figure* 1.

Photoinitiators

Traditionally, UV-curable coatings use a photoinitiator to initiate polymerization of the coating mixture. The photoinitiator absorbs UV radiation from the UV lamp, and a variety of pathways can follow. The pathways are illustrated in the Jablonski diagram (*Figure* 2).[4] The response of importance is the photoinitiator dissociating into fragments called free radicals. Two pathways for generating free radicals are depicted. One way is a single step reaction labeled PI_1 (*Figure* 3). In this reaction, the UV radiation gives the photoinitiator enough energy to cleave a bond and form two free radicals.

PI_2 is a biomolecular reaction in which the photoinitiator forms an exciplex ("an excited state complex between excited state photoinitiator and tertiary amines").[5] A hydrogen is abstracted from the tertiary

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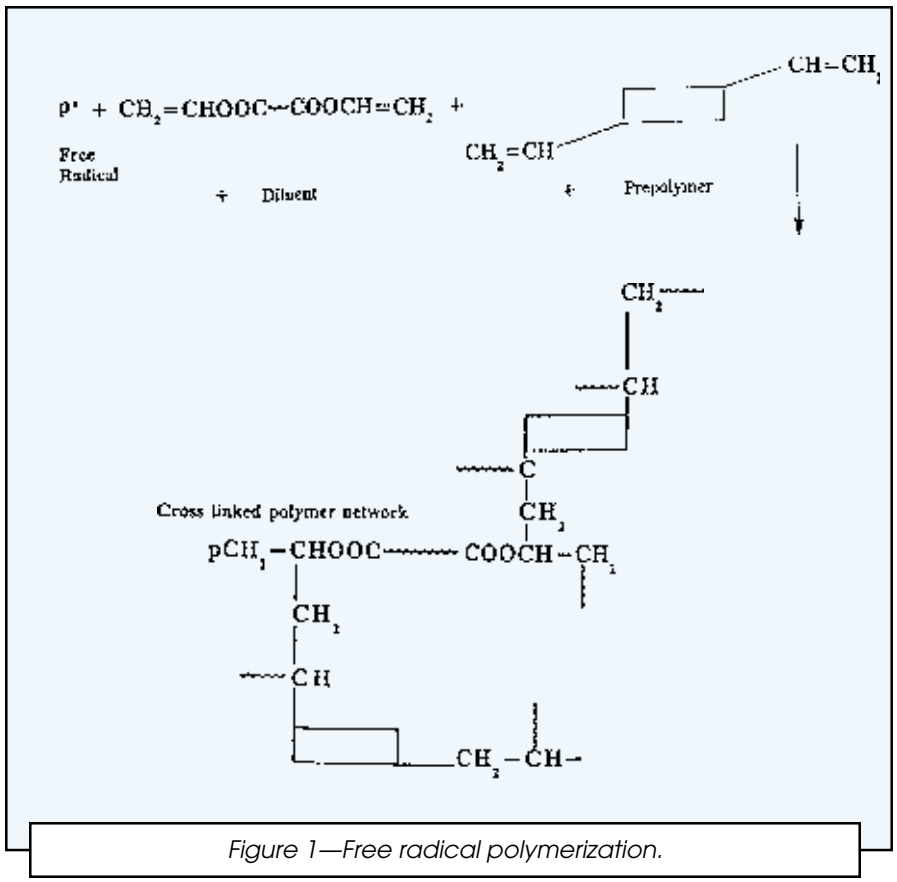


Figure 1—Free radical polymerization.

amine by the photoinitator creating two free radicals (*Figure* 4). These radicals can initiate polymerization by adding across double bonds.

Prepolymer

The prepolymer constructs the backbone of the coating. Its properties along with the reactive diluents' properties usually define the properties of the coating. Most prepolymers or oligomers are low molecular weight resins.[1] Prepolymers are divided into two types—vinyl based and non-vinyl. "Vinyl unsaturated prepolymers comprise the largest group of compounds used in UV curing....".[6] The double bond or bonds present in the prepolymer allows for rapid polymerization initiated by the photoinitiator's radicals. The non-vinyl based prepolymers are systems like the thiol-enes system.[6]

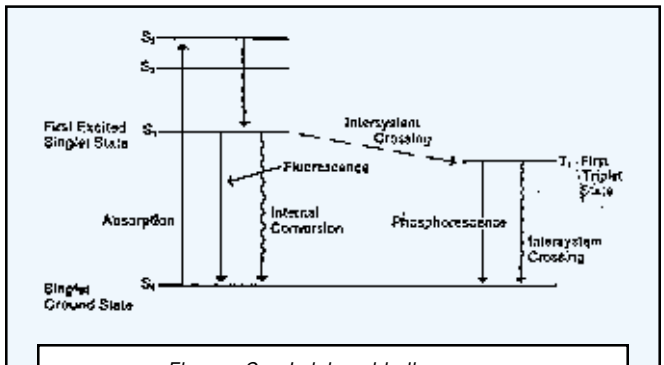


Figure 2—Jablonski diagram.

Diluents

Diluents make up an important part of the UV curable coating as well. They are monomers added to improve the properties of the pre-polymer, the cured coating, or both. These additives can be non-reactive and act like a plasticizer or as a solvent which can be flashed off before the coating is cured.[2] The diluents can also be reactive; in which case, they become incorporated into the final polymer.[5] Both function as a way to reduce the viscosity of the pre-polymer, but unlike the non-reactive diluents, the reactive ones influence the final film since they do not evaporate and are actually incorporated in the chemical structure of the coating. The reactive monomers can be monofunctional or multifunctional. Crosslinking can occur when multifunctional reactive diluents are used with difunctional prepolymers.[2] Good properties of a diluent are low volatility, low toxicity, fast curing rate, high degree of conversion, and low viscosity.[5] Low volatility results in a reduction of strong odor and increases the flash point[2] which leads to less evaporation of the monomer. For reactive diluents, low evaporation is essential because the monomers play an important role in the finished coating. The viscosity of the monomer plays an integral part in the coating mixture. It reduces the viscosity of the prepolymer and makes handling and spreading the coating mixture easier.[5]

Radiator Unit

The trials were run on a Fusion® Model F 600-10 UV curing unit with a DRS conveyor (see *Figure* 5). The unit is powered by a EPIQ 6000 power supply and has a model DRF-120 irradiator. Unlike the medium pressure mercury lamps, the xenon chloride requires a special procedure using liquid nitrogen for startup; however, it can be restarted almost immediately as long as the special procedure is followed. On the other hand, the medium pressure mercury lamps usually require a cool down period prior to restarting.

Lamps

The medium pressure mercury (MPHg) lamps and the xenon chloride (XeCl) lamps both produce UV radiation, but there are differences between the light they radiate. The medium pressure mercury lamps work by using mercury vaporized by an electric current to excite other mercury atoms and other atoms present in the

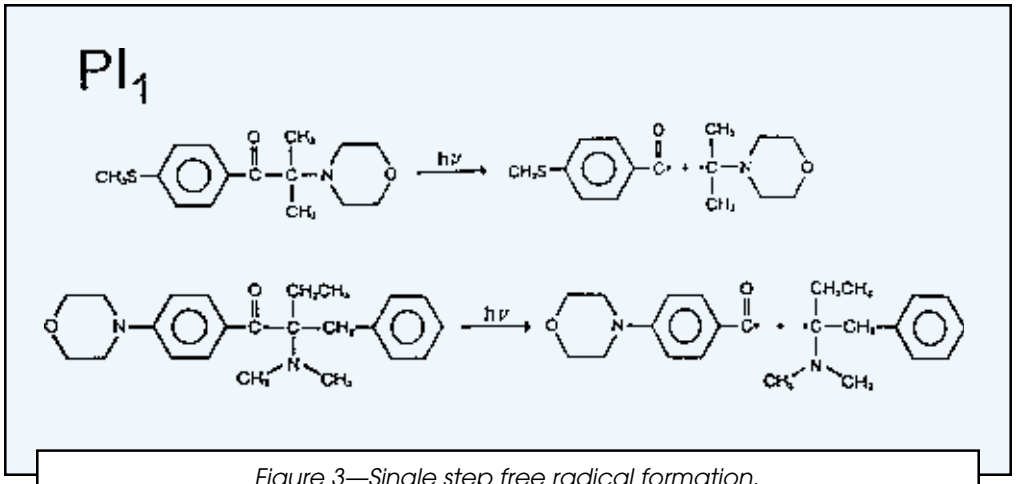


Figure 3—Single step free radical formation.

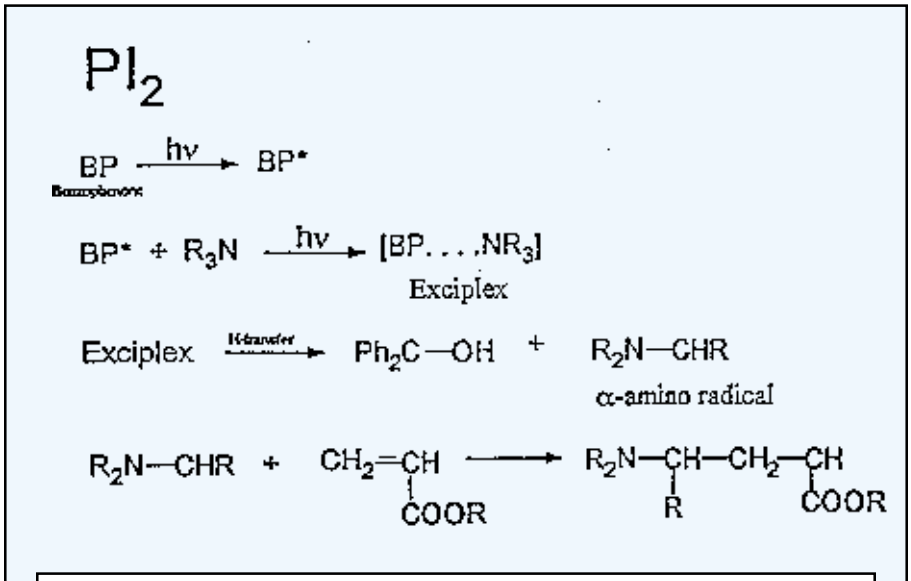


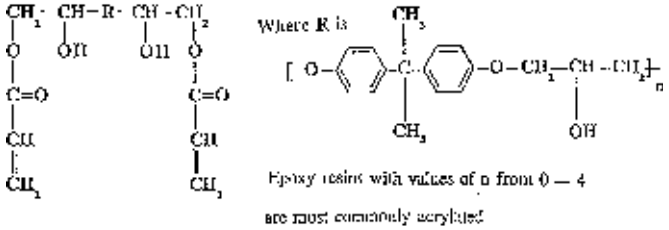
Figure 4—Bimolecular free radical formation.

bulb. "Excited mercury atoms are capable of moving from higher transition state to another, but lower transition level, and in the process a photon is emitted."[2] The wavelengths and number of photons emitted varies depending on the type of lamp. The MPHg lamp has strong bands at 361-370 nm which is an absorption band for many photoinitiators.[2] The curing rate of systems using the medium pressure mercury lamp is also affected by infrared (IR) wavelengths discharged by the ionized mercury. Data sheets on the xenon chloride lamp are not available from Fusion Systems Corporation at this time. A comparison of the emission spectrum of the XeCl and MPHg is available, however. As you will note in *Figure* 6, the XeCl lamp has significantly higher intensity in the band between 291-310 nm.[9] Many photoinitiators absorb strongly in this region; hence, the cure rate should be much higher.

Coating Composition for Curing Trials

Throughout the comparison testing of the lamps, the mixture employed consisted of 25% (weight percentage) Ebercryl® 3600 resin (diacrylate ester of a bisphenol A-type epoxy resin), 35% TRPGDA (tripropylene glycol diacrylate), 40% OTA-480 (glyceryl propoxylate triacylate), and in this mixture 0.25% to 5% photoinitiator was used. Ebercryl 3600 is the pre-polymer, TRPGDA is a difunctional diluent, and OTA-480 is a trifunctional monomer. All three samples were provided by the Radcure division of UCB Chemical Corporation.

Ebercryl 3600



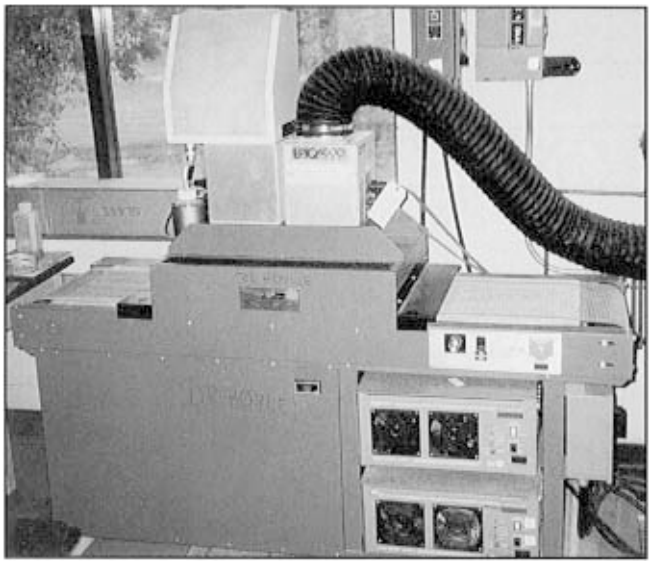


Figure 5—Fusion Model F600-10 UV curing unit.

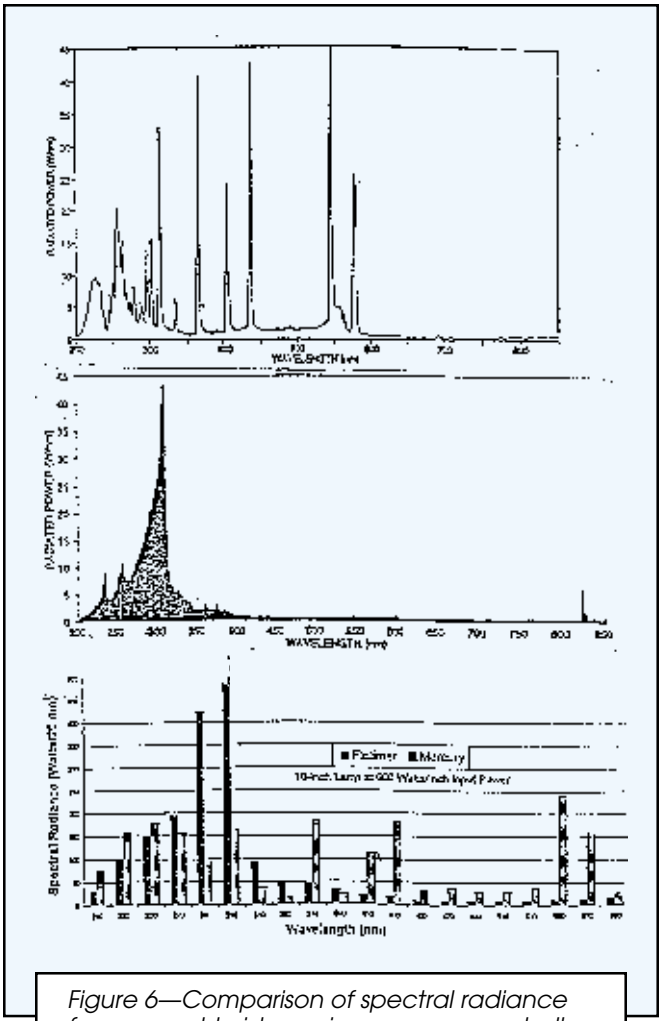
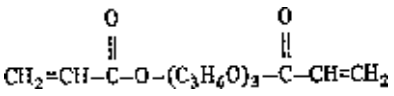
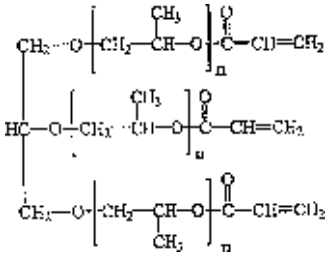


Figure 6—Comparison of spectral radiance for xenon chloride excimer vs. mercury bulbs.

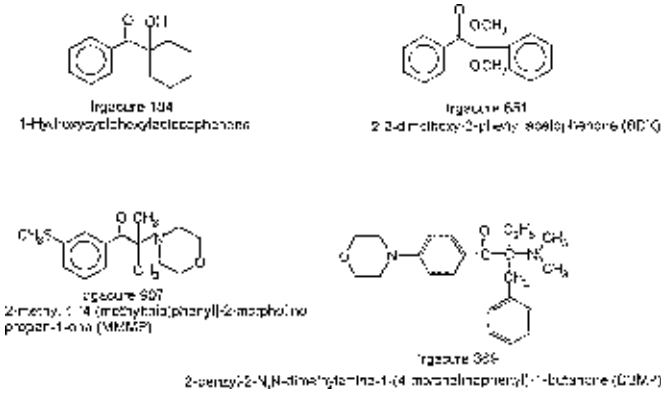
TRPGDA



OTA-480



The photoinitiators utilized and depicted blow, Irgacure® 184, Irgacure 369, Irgacure 651, and Irgacure 907, were provided by Ciba-Geigy.



PROCEDURE

The UV-curable high gloss overprint varnish components minus the photoinitator were weighed out on an electric balance and mixed in a sonicator. The desired amount of photoinitiator was then added to the mixture, and again it was sonicated. After dissolution, a small amount of the mixture was put onto a strip of special paper (called penetration charts) procured from Paul N. Gardner Co., Inc. (Gardner Form HK), metal plates, or glass plates; afterwards, a Gardner universal blade applicator was used to spread the coating mixture over the substrate at the desired thickness (0.5 to 2 mils). Next, the paper, metal plate, or glass plate was exposed to either the medium pressure mercury lamp or the xenon chloride lamp at a particular line speed. After each pass the coating was checked to see if the curing was complete by using the thumb twist test. If after 30 passes the coating was deemed still not completely cured, the exposure was discontinued, and it was recorded on the data sheet as uncured. Once the coating had apparently cured, the number of passes, speed, thickness, lamp type, and photoinitiator used was recorded on the back

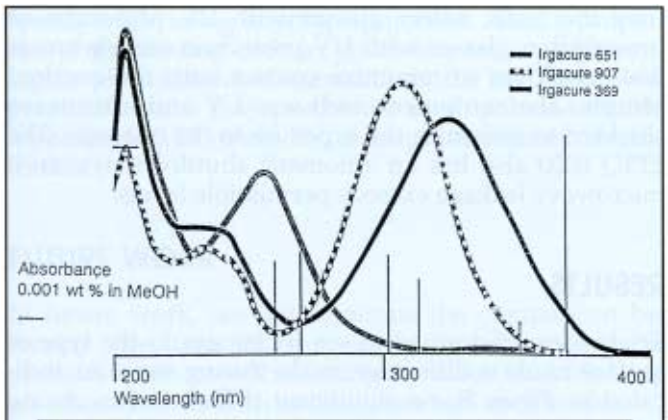


Figure 7—Comparison of three photoinitiators' absorption spectra.

and on a data sheet. To test for the degree of curing, the pencil hardness test[7] and the Powder Coating Institute's Recommended Procedure #8[8] for Solvent Cure Test were performed. The pencil hardness test uses 12 different pencils with varying graphite hardness (6B being the softest to 6H being the hardest) to measure the hardness of coating. Starting with the softest the 6B pencil is pushed forward across the coating a 45° angle with even pressure. If the film is not ruptured or scratched, the next harder pencil is tried until it ruptures or passes all 12 pencils.[7] The Solvent Cure Test (better known as the MEK rub test) involves taking a two-pound ball peen hammer and using the ball end covered in cheese cloth, which is periodically soaked by MEK, to rub up and down (a double rub) across the coating.[8] The rubbing is stopped if the film is penetrated or after 200 double rubs if there is no change in appearance and in gloss.

Safety

An important factor in dealing with any equipment or chemicals is safety. This was a concern since UV radiation can cause injury to the eyes and skin;[10] plus, TRPGDA and OTA-480 can cause skin irritation as reported in their Material Safety Data Sheets. Gloves and safety glasses were worn and the area was well ventilated to reduce the risk of chemicals passing through the skin and to minimize inhalation of vapors. When run-

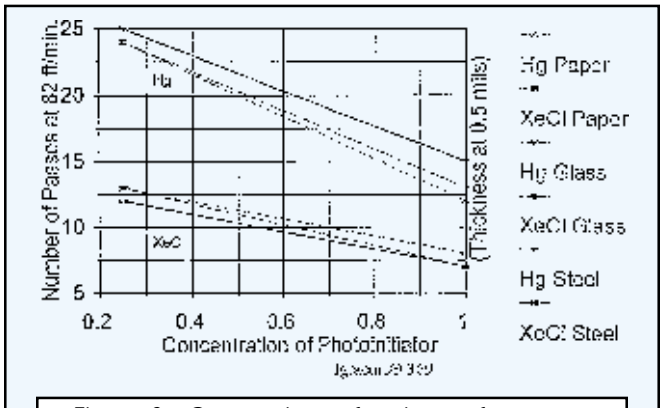


Figure 8—Comparison of curing surfaces between the XeCl and Hg lamps.

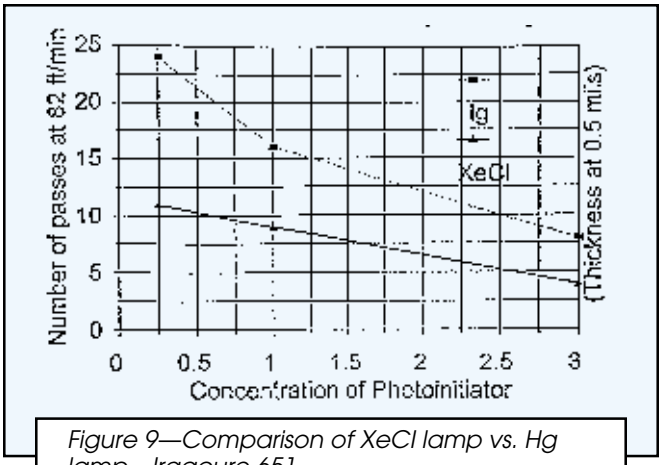


Figure 9—Comparison of XeCl lamp vs. Hg lamp—Irgacure 651.

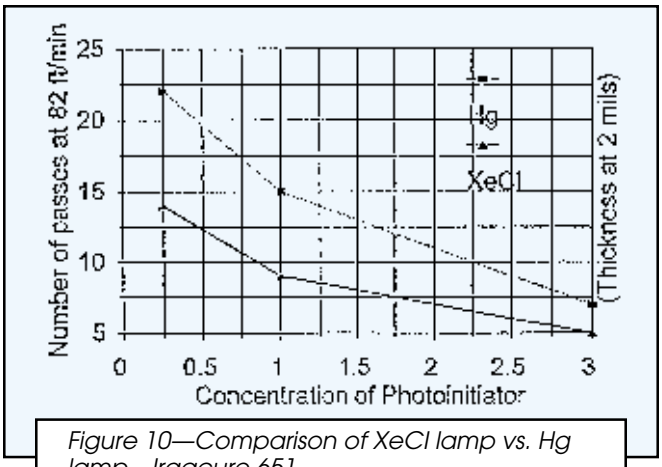


Figure 10—Comparison of XeCl lamp vs. Hg lamp—Irgacure 651.

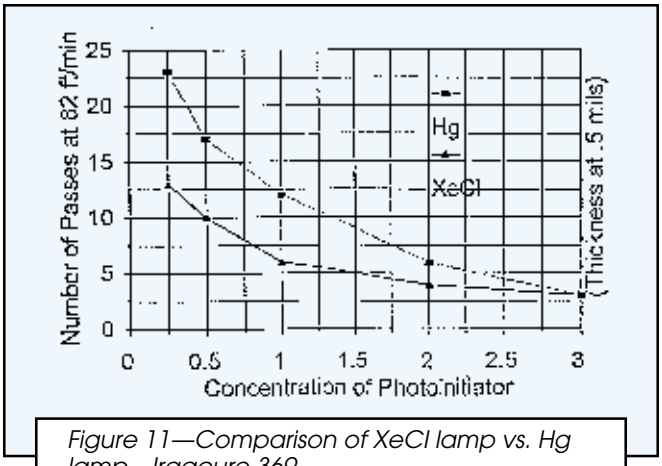


Figure 11—Comparison of XeCl lamp vs. Hg lamp—Irgacure 369.

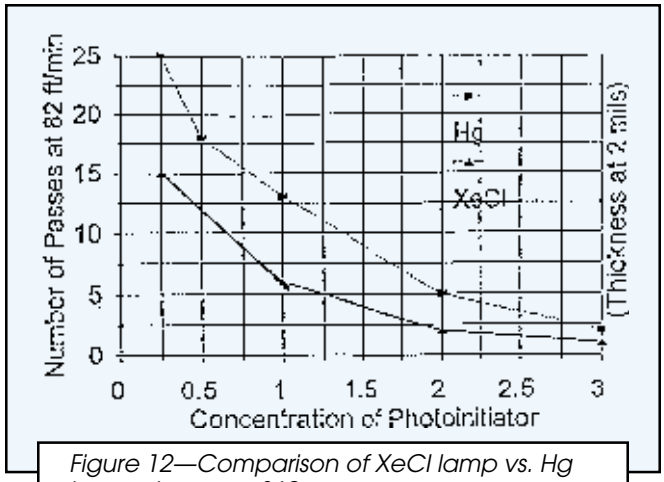


Figure 12—Comparison of XeCl lamp vs. Hg lamp—Irgacure 369.

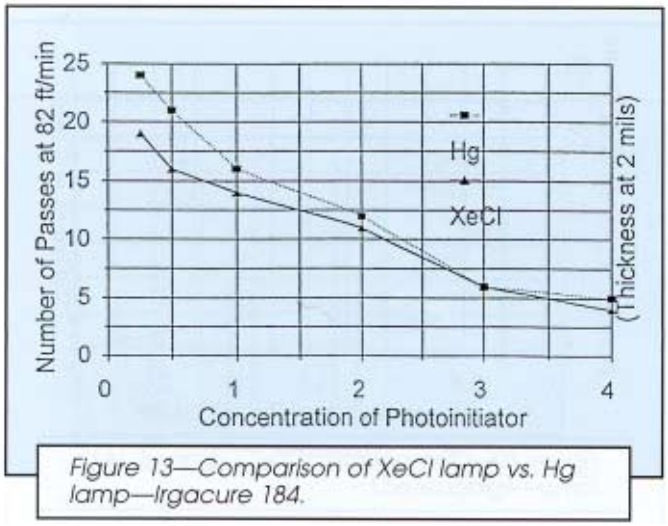


Figure 13—Comparison of XeCl lamp vs. Hg lamp—Irgacure 184.

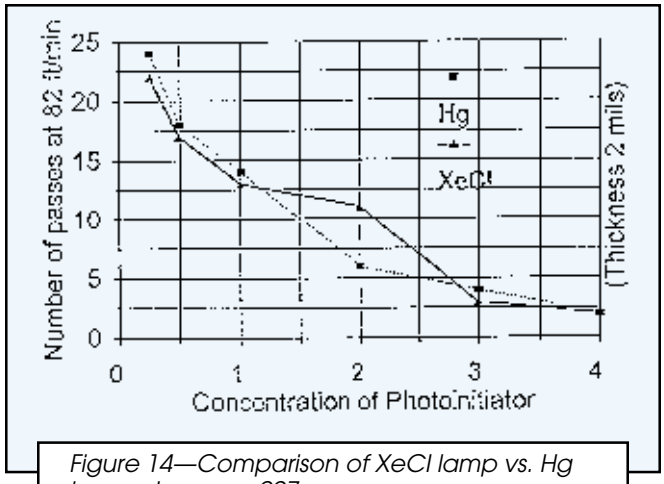


Figure 14—Comparison of XeCl lamp vs. Hg lamp—Irgacure 907.

ning the trials, safety glasses with UV protection or prescription glasses with UV protection were worn as well as gloves to minimize contact with the uncured sample. The equipment itself was UV and microwave shielded to minimize the exposure to the operator. The EPIQ 6000 also has an automatic shutdown system if microwave leakage exceeds permissible levels.

RESULTS

Trials were performed to see if changes in the type of surface made a difference in the curing time. As indicated in *Figure* 8, no significant differences in curing times were evident when the substrate was changed from penetration charts to glass to metal. Therefore, penetration charts were cut to an appropriate size and used for convenience and for economic reasons.

The next step was to try two thicknesses to see if thickness would significantly affect the curing rate. Using Irgacure 651 and Irgacure 369, 0.5 mils and 2 mils samples were tested. See *Figures* 9-12. Only minor differences in the curing times were evident between the two thicknesses.

Two other photoinitiators were tested at a range of concentrations, generally from 0.25% to 4%. Irgacure 184 was tested first. *Figure* 13 depicts the results. When the photoinitiator is changed to Irgacure 907, it exhibited similar results to the Irgacure 184 (*Figure* 14). Although, Irgacure 184 and Irgacure 907 did not exhibit as significant a difference in curing times between the two lamps, the xenon chloride lamp was again faster except for one anomalous value which we are re-investigating.

CONCLUSIONS

The xenon chloride lamp has advantages for curing a clear coating over the medium pressure mercury lamp. At the low concentrations (0.25%), the XeCl was approximately 90% faster, meaning it took the average of 11.67 less passes then the MPHg. A one percent concentration of photoinitiator was roughly 80% faster on all of the substrates. The thickness results also support the XeCl lamp as being faster in curing time with slightly lower percentage on average, 80% faster with a low concentration of photoinitiator (Irgacure 651) and 65% faster at the higher concentration. When the photoinitiator was changed to Irgacure 369, the xenon chloride lamp allowed for less passes (75% faster) at low concentrations and an equal number of passes high concentrations with the 0.5 mils thickness. With the other two photoinitators (Irgacure 184 and Irgacure 907), the xenon chloride lamp, again, proved to be faster in curing than the mercury lamp when compared using the same thickness and speed of the conveyor belt. The xenon chloride lamp was about 25% faster at all of the concentrations using Irgacure 184.

New technology such as the development of the xenon chloride lamp is important to industry which seeks to increase efficiency and improve the properties of its coatings. The xenon chloride lamp can increase the line

speeds while using existing equipment. Also, if properties of the coating such as yellowing are a problem at higher photoinitator concentrations, the XeCl lamp will permit the same line speed to be used with one-fourth, for example 0.25 versus 1%, of the photoinitiator concentration.

FUTURE WORK

In future work, we will continue the comparison between the two lamps using combinations of photoinitiators as well as testing the xenon chloride lamp on other systems such as thiol-enes and maleimides.

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