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EFFECT OF ATMOSPHERIC AND LABORATORY IRRADIATION ON ATTENUATED TOTAL REFLECTANCE SPECTRA OF ORGANIC COATINGS

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CIVIL ENGINEERING LABORATORY
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By

Peter J. Hearst, Ph D

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Attenuated Total Reflectance (ATR) spectra were obtained before and after irradiation of coating films as part of an investigation to develop better accelerated test methods for determining coating performance. The coatings included alkyd, oil, vinyl-alkyd, vinyl copolymer, partially hydrolyzed vinyl copolymer, epoxy-amine, and epoxy-polyamide films. Clear and pigmented films had previously been irradiated in air with a mercury arc and with

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INTRODUCTION

The determination of coating performance by means of accelerated tests was investigated at the Civil Engineering Laboratory.

Accelerated tests for coatings, as typically employed in industry, consist of the exposure of specimens to extreme artificial environments followed by visual inspection of the results. The goal of the CEL investigations was to determine what types of changes occur in coatings that would be measurable and would thus provide quantified data that might be useful for performance predictions.

The CEL studies included an investigation of the photodegradation products of organic coatings. The results of investigations of the volatile products obtained from the irradiation of various clear and pigmented organic coating films have been reported [1-4].

The CEL studies also included investigations of surface change resulting from the photodegradation of organic coatings. Since much of the deterioration--and especially the photodegradation--of coatings and plastics occurs primarily at the surface, it should be possible to relate changes at the surface to the performance of the coatings. Attenuated total reflectance (ATR) spectra, or internal reflection spectra, give infrared absorption data for thin surface layers. Such spectra should, therefore, be valuable in following chemical changes that occur on the surface of irradiated coatings.

The results of prior investigations of the effects on the ATR spectra of mercury-arc and xenon-arc irradiation of clear and pigmented coating films have been reported [5, 6]. It was found that, in general, mercury-arc irradiation of clear films produced the greatest changes in the ATR spectra. Lesser effects were produced by the mercury-arc irradiation of pigmented films and still lesser effects were produced by xenon-arc irradiations. Xenon-arc irradiations were found to have greater effects on the pigmented films than on the clear films. The greatest effects were noted in the region of 1600 to 1800 cm^{-1}, probably because of the formation of carbonyl compounds in the degradation process. These changes were less noticeable in coatings which already had considerable carbonyl absorption before irradiation. Among the chief generic types of coatings studied, that is, alkyd, vinyl, and epoxy films, the epoxy films, which had the lowest initial carbonyl absorption, showed the greatest changes.

It was of interest to determine whether exposure to atmospheric sunlight would result in changes similar to those produced by xenon-arc irradiation (as might be expected because of the similarity of the light sources), or whether there would instead be more similarity with the effect of mercury-arc irradiation. Several clear and pigmented coating films were exposed to the atmosphere for a period of 5 months. Some pigmented films were also exposed for a longer period to xenon-arc irradiation in a Weather-Ometer. The results of these exposures and the results of some additional exposures to mercury-arc and shorter xenon-arc irradiation are reported below. Since these results are supplementary to those reported in NCEL Technical Report R-479 [5], the material is presented in the same format, and details previously presented will not be repeated, except as necessary for clarity. These new results have been summarized in the literature [7], but they are presented here in greater detail.

EXPERIMENTAL METHODS

Preparation of Individual Films

The preparation of most of the clear and pigmented films by blade application to Teflon or Kynar sheets was previously described [5]. Two additional films were prepared. One was an oil paint film, Federal Specification TT-E-102, which had a dry-film thickness of 6.5 mils (135 microns). The other film was a vinyl film made from a typical vinyl chloride-vinyl acetate copolymer containing approximately 86% vinyl chloride and 14% vinyl acetate; the film was 2.0 mils (50 microns) thick.

Exposure Conditions

A quartz exposure chamber (essentially an infrared gas cell 100 mm long and 40 mm in diameter with Irtran 2 windows) was used for the 6-hour mercury-arc and 54-hour xenon-arc irradiation [5].

The 500-hour xenon-arc irradiations were performed in the Weather-Ometer without an exposure chamber. The films were clamped onto white paper that was placed on a metal panel, and this in turn was placed on a sample rack. For these longer exposures, the distance from the lamp to the sample was increased from 12 inches to 18 inches. A pyrheliometer with the element placed 18 inches from the xenon-arc indicated a total light intensity of 1.53 cal cm^{-2} min^{-1}, or langleys per minute, over a period of 500 hours; the total irradiation was, therefore, about 45,000 langleys. The 54-hour irradiation at 12 inches from the arc therefore had an intensity of 3.45 cal cm^{-2} min^{-1} and a total irradiation of about 11,000 langleys. The increased exposure time at a reduced light intensity, thus, had a net effect of producing approximately a four-fold increase in total irradiation.

For the 5-month atmospheric exposure, the films were mounted on a plastic holder as shown in Figure 1. This holder was so designed that one half of each film could be removed for determination of the spectrum and the other half could then be exposed for an additional period of

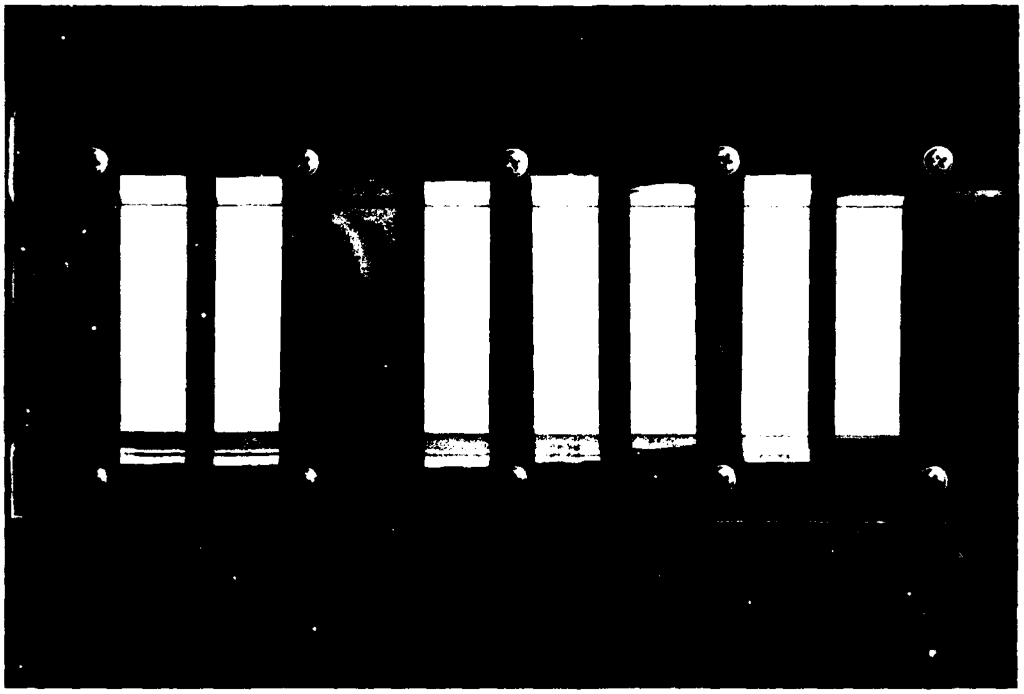

Figure 1. Coating film holder.

time. The exposure was at Port Hueneme, California at about 34° North latitude. The sample holder was held at a 30-degree angle from the horizontal, and it faced south to obtain essentially maximum solar radiation. The average solar radiation on a surface facing in this direction was approximately 12,000 langleys per month, as measured with a pyrheliometer. The films were held approximately 30 feet above ground level to reduce the effect of dust, and they were washed periodically with a stream of water to reduce the accumulation of dust.

Attenuated Total Reflectance Spectra

The spectra were obtained, as before, with a single reflection KRS-5 prism. A prism angle of 50 degrees was used for pigmented films, and a prism angle of 45 degrees for clear films. The ATR spectra of the films that showed significant changes are reproduced in this report. Spectra that showed no significant changes and those which have been reported before [5] generally are not reproduced.

DISCUSSION OF RESULTS

Nature of the Investigation

Prior investigations have shown that considerable effects in the ATR spectra are obtained with mercury-arc irradiation, but that comparatively small effects are produced by xenon-arc irradiation [5]. The newer investigation was performed to determine whether longer xenon-arc irradiation would produce more significant results and whether the results of atmospheric exposure were similar to xenon-arc exposure results.

The determination of the volatile products from the atmospheric exposures would have complicated the experimental conditions; therefore, it was not attempted. In the longer xenon-arc irradiations such an attempt was likewise omitted.

The atmospheric exposures were performed both with clear films and with pigmented films. Quite a few of the clear films and one of the pigmented films were lost from the plastic holder before the 5-month exposure period was completed. The losses apparently were caused by environmental effects, such as wind and rain, on the deteriorating films. The greater loss of the clear films may have been due to the greater brittleness which was produced in these films during atmospheric exposure.

General Results

Even the 500-hour xenon-arc irradiation had relatively little effect on the ATR spectrum of the pigmented alkyd film. Similar irradiation of a pigmented vinyl film reduced the peak heights slightly. Irradiation of a pigmented epoxy film also produced a general reduction of peak heights, but the greatest effect was the production of strong peaks at 1730 and 1655 cm^{-1}; these were considerably greater than those produced by the 54-hour xenon-arc irradiation.

The 5-month atmospheric exposure generally had effects that were similar to those of the xenon-arc irradiation, but the relative effects differed for different generic types of coatings. The atmospheric exposure had a greater effect in reducing the ATR peaks of a pigmented alkyd film than did the 500-hour xenon-arc irradiation. Both exposures produced about the same slight peak reduction in the ATR spectra of pigmented vinyl films. The atmospheric exposure had a lesser effect in producing strong peaks at 1720 and 1655 cm^{-1} in the ATR spectra of epoxy films than did the 500-hour xenon-arc irradiation.

The relative effectiveness of the two exposures in producing photodegradation could not have been predicted from the total irradiation of the two sources as measured by a pyrheliometer. The 5-month atmospheric exposure was equivalent to approximately 60,000 langleys; the 500-hour xenon-arc exposure was equivalent to approximately 45,000 langleys. The atmospheric exposure included morning and evening light with a lower portion of ultraviolet light, but the xenon-arc included considerable infrared light.

Results With Individual Films

Additional results for the various vehicles under the various types of irradiation in clear and pigmented films are discussed below. They are also listed in Table 1 to allow a better comparison of results.

Small quantitative differences in the ATR spectra may not be significant because of inherent difficulties in the method. Differences in the contact obtained between the sample and the prism can affect the spectrum, and small deviations in the angle of incidence, especially when this is close to the critical angle, can have a considerable effect. Thus, for a clear alkyd film with an experimentally determined critical angle of 37 degrees, the absorbance of the major peak at 1720 cm^{-1} varied as follows:

Angle of Incidence (deg)	Absorbance
49	0.40
44	0.59
41	0.79
39	0.90

Alkyd Films. The greatest changes in the ATR spectra of the alkyd films were produced by the mercury-arc irradiation of the clear alkyd film. The principal changes occured at 1770 cm^{-1} and at 1650 cm^{-1} and were presumably due to increased carbonyl absorption. Other changes include the disappearance of the doublet at 1580 and 1600 cm^{-1}, the appearance of a new peak at 1165 cm^{-1}, an increase in absorption near 1000 cm^{-1} (probably due to carbon-oxygen linkages), an increase in absorption at 3400 cm^{-1} (probably due to hydroxyl groups), and a general reduction in peak heights. These changes are shown in Figure 2, which is reproduced from Reference 5.

The 5-month atmospheric exposure of the alkyd films produced only slight decreases in the peaks, as shown for the pigmented film in Figure 3. The pigmented film showed a slight change in color during the same atmospheric exposure from white to a light egg-shell color. The 500-hour xenon-arc irradiation produced a negligible effect, which is not illustrated.

Oil Paint Films. Only the pigmented oil paint was studied, because removal of the pigment resulted in a vehicle that did not form a satisfactory film. The general results are shown in Table 1. The atmospheric exposure produced some yellowing and considerable loss in gloss. It produced strong decreases in peak heights. An exception was the peak at 1020 cm^{-1}, which presumably was due to carbon-oxygen linkages; it actually increased in height, as shown in Figure 4.

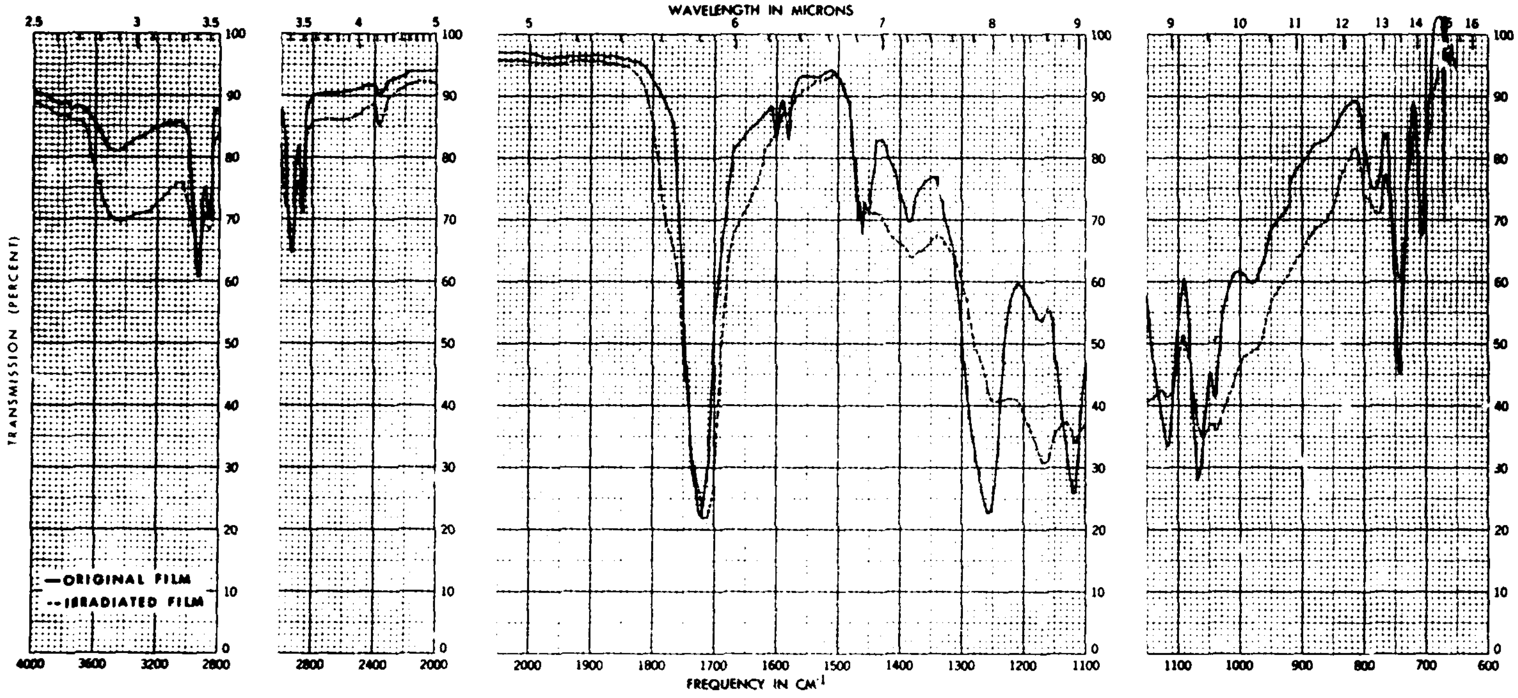

Figure 2. Effect of mercury-arc irradiation on the ATR spectrum of a clear alkyd film.

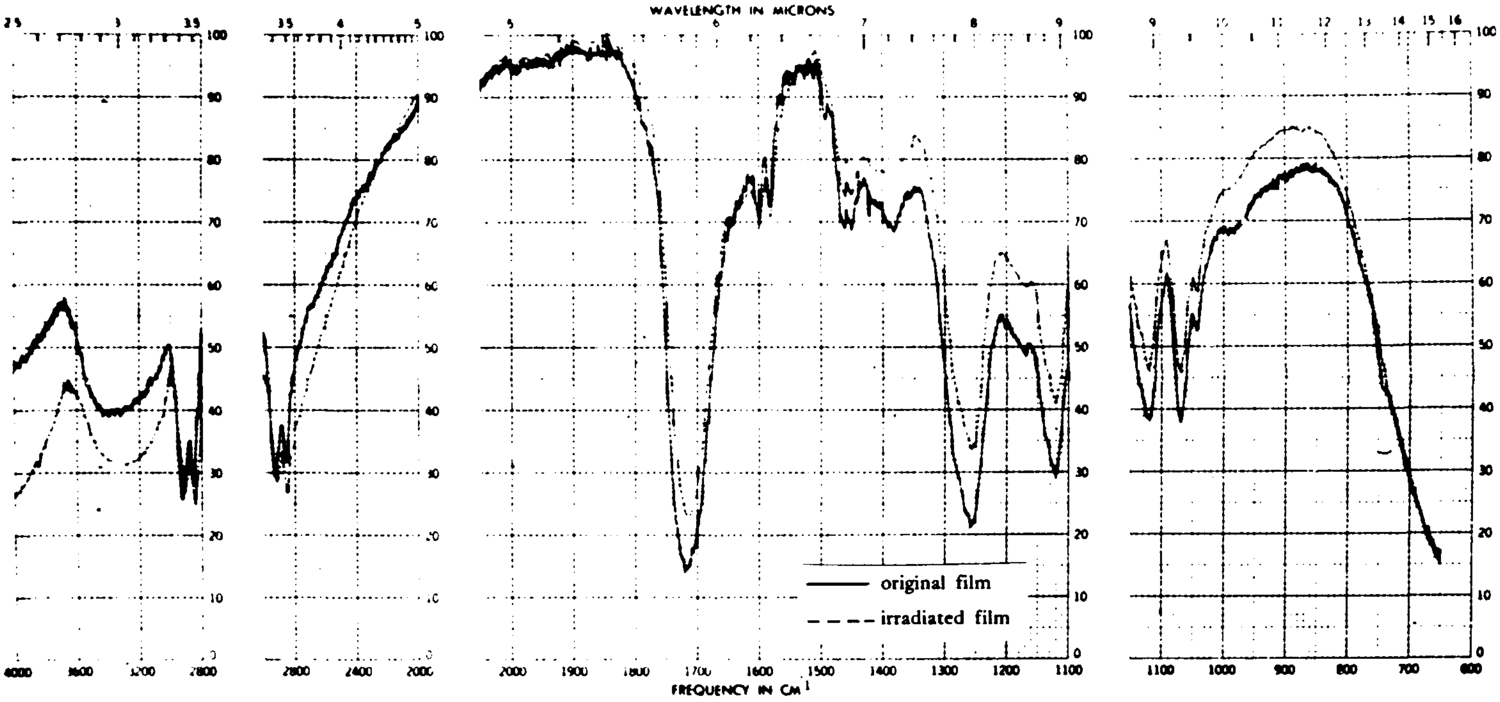

Figure 3. Effect of atmospheric exposure on the ATR spectrum of a pigmented alkyd film.

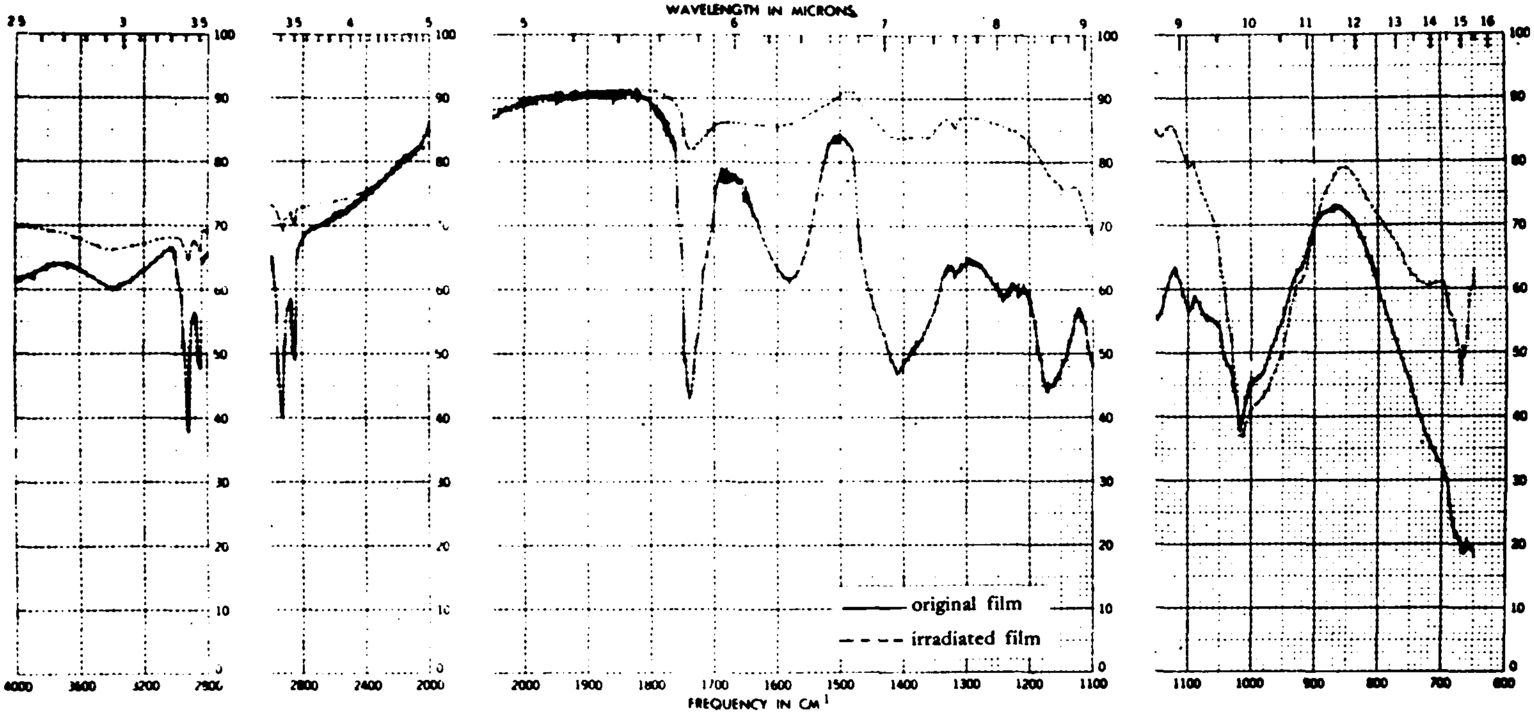

Figure 4. Effect of atmospheric exposure on the ATR spectrum of an oil paint.

Table 1. Effect of Irradiation on ATR Spectra of Coating Films

[The four-digit numbers are the frequencies (in cm^{-1}) in the ATR spectra.]

Type of Film	6-Hour Mercury Arc		54-Hour Xenon Arc		5-Month Atmospheric	
	Clear Film	Pigmented Film	Clear Film	Pigmented Film	Clear Film	Pigmented Film
Alkyd	Wider at 1600-1800 Peak at 1165 Decreased peaks	Slightly decreased peaks	No significant change	No significant change[a]	Slightly decreased peaks	Slightly decreased peaks
Oil Paint	–	Decreased peaks	–	No significant change	–	Strongly decreased peaks except at 1020
Vinyl Alkyd	Wider at 1600-1800 Peak at 1165 Decreased peaks	Decreased peaks	No significant change	Strong decrease	–	Moderate decrease[b]
Vinyl	Strong increase 1600-1800 Shoulder at 1625 Decreased peaks	–	No significant change	No significant change[c]	No significant change	Slightly decreased peaks
Vinyl (hydrolyzed)[d]	Strong increase 1600-1800 Shoulder at 1625 Decreased peaks	Increase 1740 & 1700 Decreased peaks	Slight increase 1740 Slightly decreased peaks	Decreased peaks	–	Slight increase 1740 Slightly decreased peaks
Epoxy (amine-cured)	Strong increase 1720 & 1655 ($\Delta A \sim 0.17$ & ~ 0.14) Decreased peaks	Strong increase 1720 & 1655 ($\Delta A \sim 0.10$ & ~ 0.10) Little other effect	Increase at 1655 ($\Delta A \sim 0.04$) No other effect	Increase at 1655 ($\Delta A \sim 0.04$) No other effect	Increase 1720 & 1655 ($\Delta A \sim 0.04$ & ~ 0.04) Strongly decreased peaks	Increase 1720 & 1655 ($\Delta A \sim 0.04$ & ~ 0.03) Slightly decreased peaks
Epoxy (polyamide-cured)	Strong increase 1720 & 1655 ($\Delta A \sim 0.12$ & ~ 0.08) Decreased peaks	Strong increase 1720 & 1655 ($\Delta A \sim 0.12$ & ~ 0.04) Decreased peaks	Slight increase 1655 ($\Delta A \sim 0.02$) No other effect	Slight increase 1720 & 1655 ($\Delta A \sim 0.03$ & ~ 0.02) No other effect[e]	–	Slight increase 1720 & 1655 ($\Delta A \sim 0.03$ & ~ 0.02) Decreased peaks

[a] 500-hr xenon arc – no significant change.

[b] 2-month atmospheric irradiation.

[c] 500-hr xenon arc – slightly decreased peaks.

[d] Partially hydrolyzed vinyl chloride – vinyl acetate copolymer.

[e] 500-hr xenon arc – strong increase 1720 & 1655 ($\Delta A \sim 0.10$ & ~ 0.07).

The mercury-arc irradiation produced smaller decreases for all the major peaks, including the one at 1020 cm^{-1}, and the xenon-arc irradiation produced no significant change. The greater relative effect of the atmospheric exposure may primarily have been due to the poor contact obtained with the rough surface of the exposed paint and could also have been due to other differences in the environment. Greater similarity in the effect of atmospheric irradiation with that of mercury-arc irradiation as opposed to that of xenon-arc irradiation is not necessarily indicated.

Vinyl-Alkyd Films. In general, the effects on the clear vinyl-alkyd films were between those observed for the alkyd films and the vinyl films. The changes produced by the mercury-arc irradiation are shown in Figure 5, which is reproduced from Reference 5. The general decrease in peak heights of the pigmented films was greater than that of the corresponding alkyd or vinyl films; this difference might be because of the gray pigment of these films. The pigmented vinyl-alkyd film survived 2 months of atmospheric exposure, but was lost before the 5-month period was completed, apparently because of excessive film deterioration.

Vinyl Films. Two types of vinyl films were studied. One was a vinyl chloride-vinyl acetate copolymer containing about 14% vinyl acetate. The other was a partially hydrolyzed copolymer containing the equivalent of about 3% vinyl acetate and about 6% vinyl alcohol. The higher acetate content of the former film was evidenced by increased absorption peaks, notably at 1740 cm^{-1} and 1235 cm^{-1}, as shown in Figures 6 and 7.

The most significant changes produced in the ATR spectra of the vinyl films were in the carbonyl region, as indicated in Table 1. The greatest changes were produced by mercury-arc irradiation, which produced strong shoulders at 1770 and 1630 cm^{-1} and a strong increase in the peak at 1715 cm^{-1}. These changes were much more evident in the spectrum of the hydrolyzed clear film (as shown in Figure 8, which is reproduced from Reference 5), which had less initial carbonyl absorption than the unhydrolyzed film. There was also a slight increase at 3300 cm^{-1}, which may have been caused by hydroxyl groups.

The 5-month atmospheric exposure produced a slight decrease in the absorption peaks of the pigmented vinyl film (Figure 6), which for the partially hydrolyzed film was accompanied by a slight increase in absorption at 1740 cm^{-1} (as shown in Figure 7). There was little change in color or gloss of the film. The effect of the 500-hour xenon-arc irradiation was similar to that of the atmospheric exposure, resulting in a slight decrease in the peaks.

Epoxy Films. Two types of epoxy films were studied. One was amine-cured, the other was polyamide-cured. The former was affected to a greater extent by irradiation, as shown in Table 1. This difference may have been due to the greater epichlorohydrin-bisphenol A content of the amine-cured coating.

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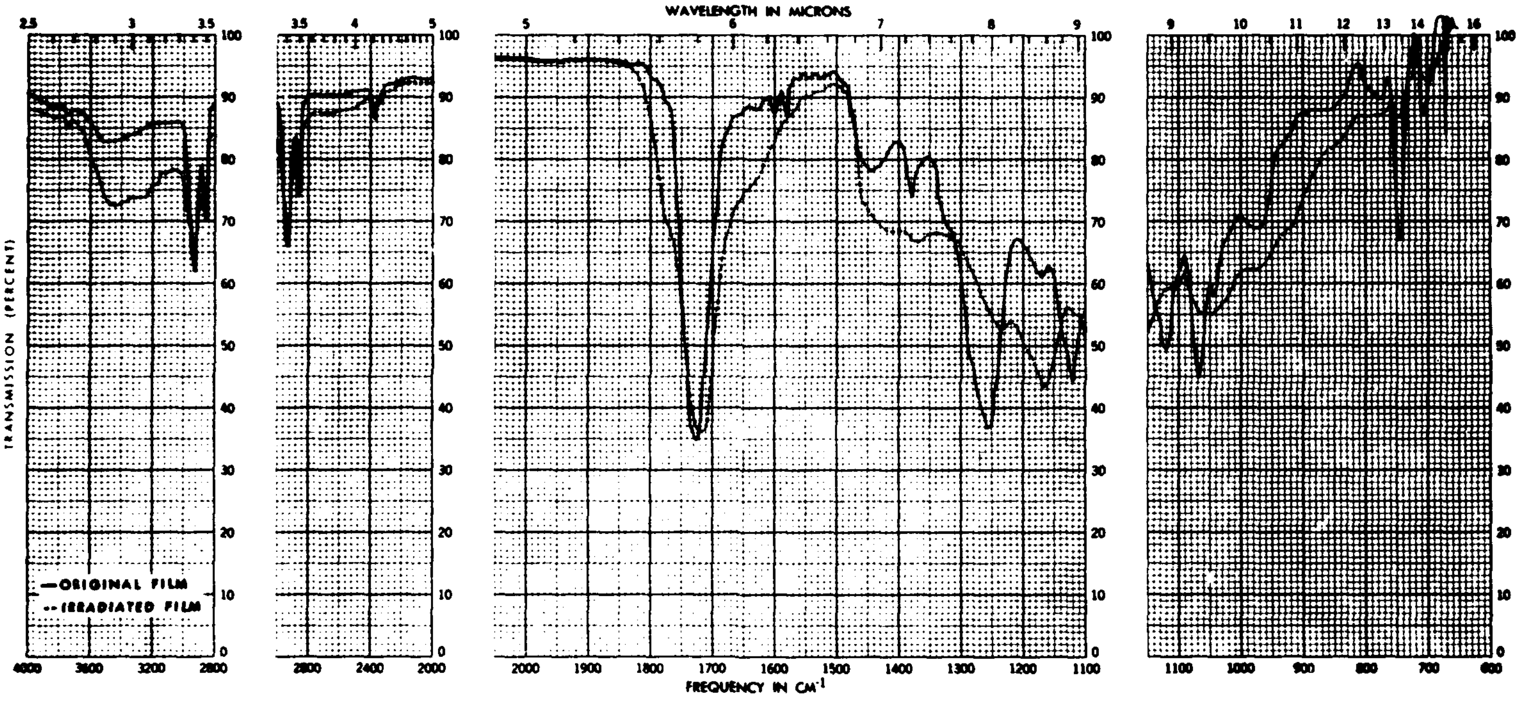

Figure 5. Effect of mercury-arc irradiation on the ATR spectrum of a clear vinyl-alkyd film.

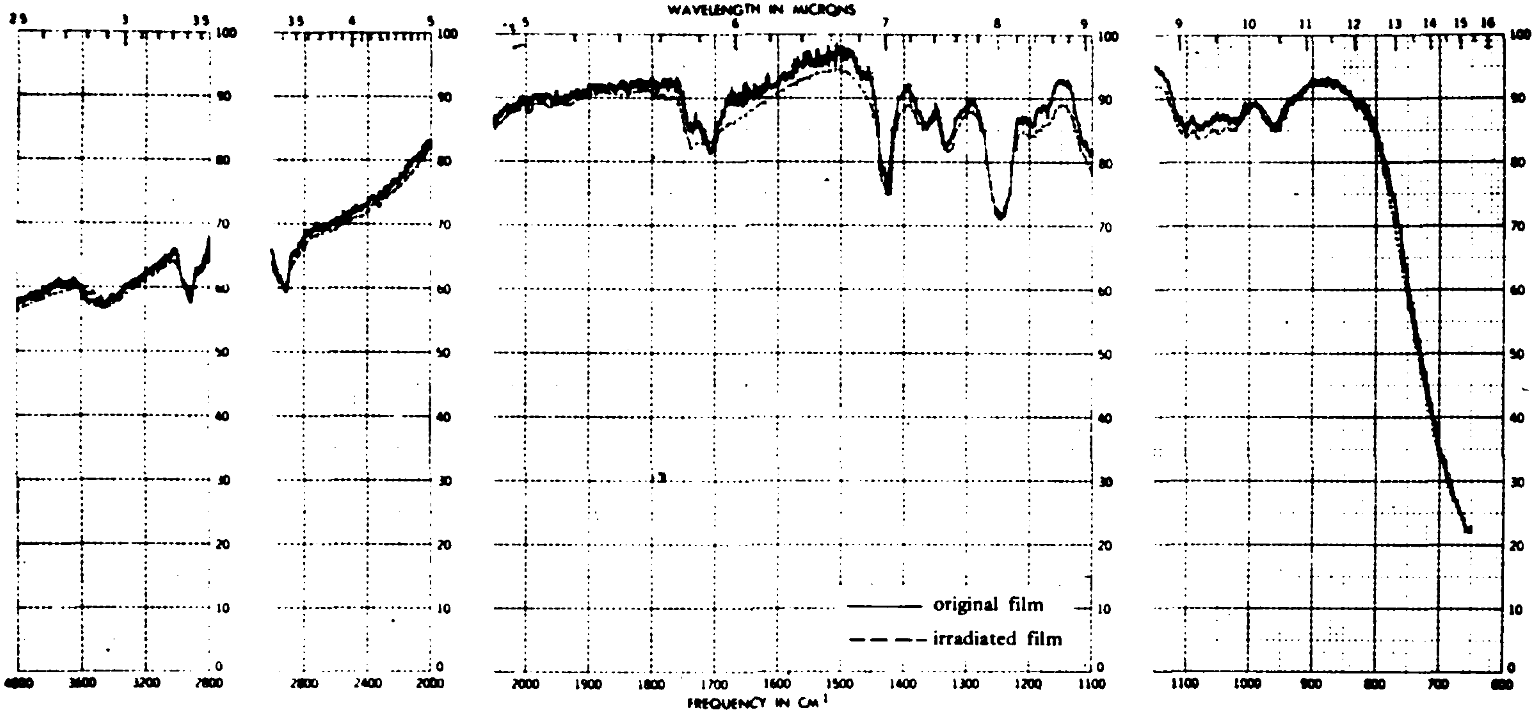

Figure 6. Effect of atmospheric exposure on the ATR spectrum of a pigmented vinyl film.

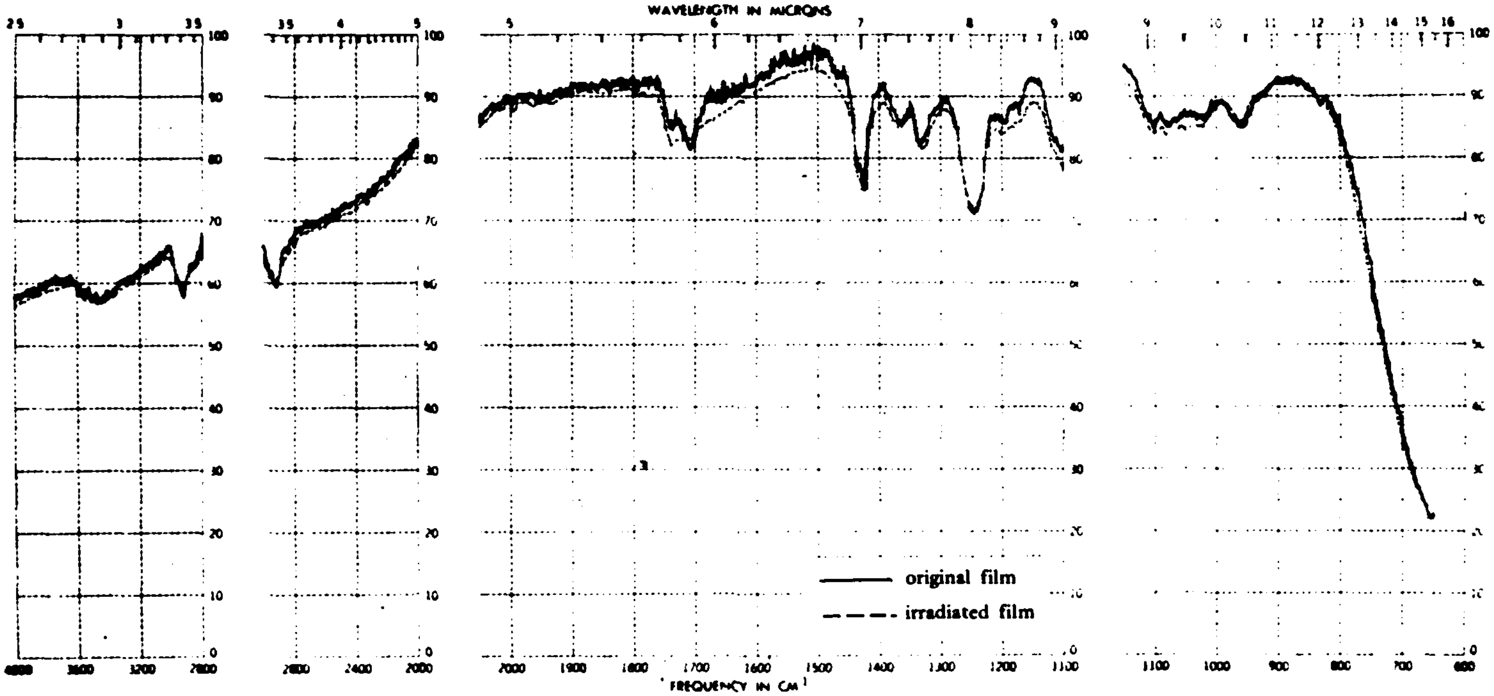

Figure 7. Effect of atmospheric exposure on the ATR spectrum of a pigmented, partially hydrolyzed vinyl film.

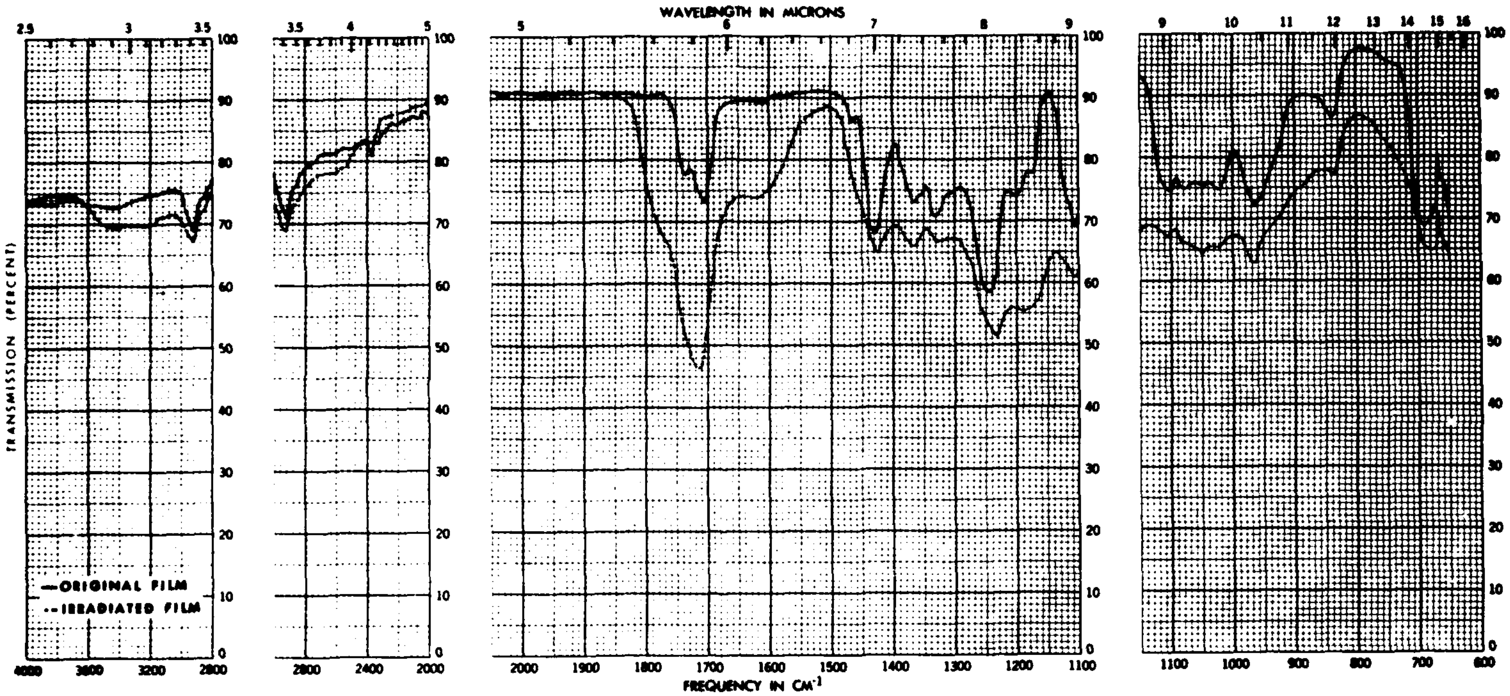

Figure 8. Effect of mercury-arc irradiation on the ATR spectrum of a clear, partially hydrolyzed vinyl film.

The greatest effect on the ATR spectra of the epoxy films was again produced by the mercury-arc irradiation of the clear films, as noted in Table 1 and as shown in Figures 9 and 10 (reproduced from Reference 5). The major change was the formation of two peaks at 1720 cm^{-1} and 1655 cm^{-1} in the carbonyl region of the spectrum. These peaks, or at least that at 1655 cm^{-1}, were produced as a result of each of the irradiation experiments with the epoxy films.

For the epoxy films, the effect of 54-hour xenon-arc irradiation [5] was about as strong as the effect of the 5-month atmospheric exposures, shown in Figures 11 and 12. The effect of the 500-hour xenon-arc irradiation was considerably greater, as shown in Figure 13. The atmospheric exposure produced a yellow egg-shell color in the pigmented epoxy films, and considerably reduced the gloss.

The increased absorbance at 1720 cm^{-1} and 1655 cm^{-1} was, in general, proportional to the total irradiation received. The change in absorbance, ΔA, was calculated from the percent transmission at the peak, T, and the percent transmission at the baseline at the same frequency, T_B, by using the equation derived as follows (where T_o is 100% tranmission and A_B is the absorbance at the baseline):

$$A = \log_{10} (T_o/T)$$

$$\Delta A = A - A_B = \log_{10} (T_o/T) - \log_{10} (T_o/T_B)$$

$$\Delta A = \log_{10} (T_B/T)$$

The average increase in absorbance of the peaks at 1720 cm^{-1} and 1655 cm^{-1} under xenon-arc irradiation was as follows:

54 hours or about 11,000 langleys	$\Delta A = \sim 0.03$
500 hours or about 45,000 langleys	$\Delta A = \sim 0.09$

The average increase under atmospheric exposure was:

2 months or about 24,000 langleys	$\Delta A = \sim 0.014$
5 months or about 60,000 langleys	$\Delta A = \sim 0.031$

The comparatively lesser effect of an equivalent number of langleys of atmospheric exposure was probably due to the fact that the total measured atmospheric irradiation included morning and evening light, which has a relatively lower content of ultraviolet light. The ultraviolet light is primarily responsible for photodegradation, especially for photodegradation at the coating surface.

Significance of the Results

Atmospheric exposure produced results which were much more similar to those of the xenon arc than to those of the mercury arc. Correlations with performance would, therefore, be expected to be greater for the results of xenon-arc irradiation than for mercury-arc irradiation.

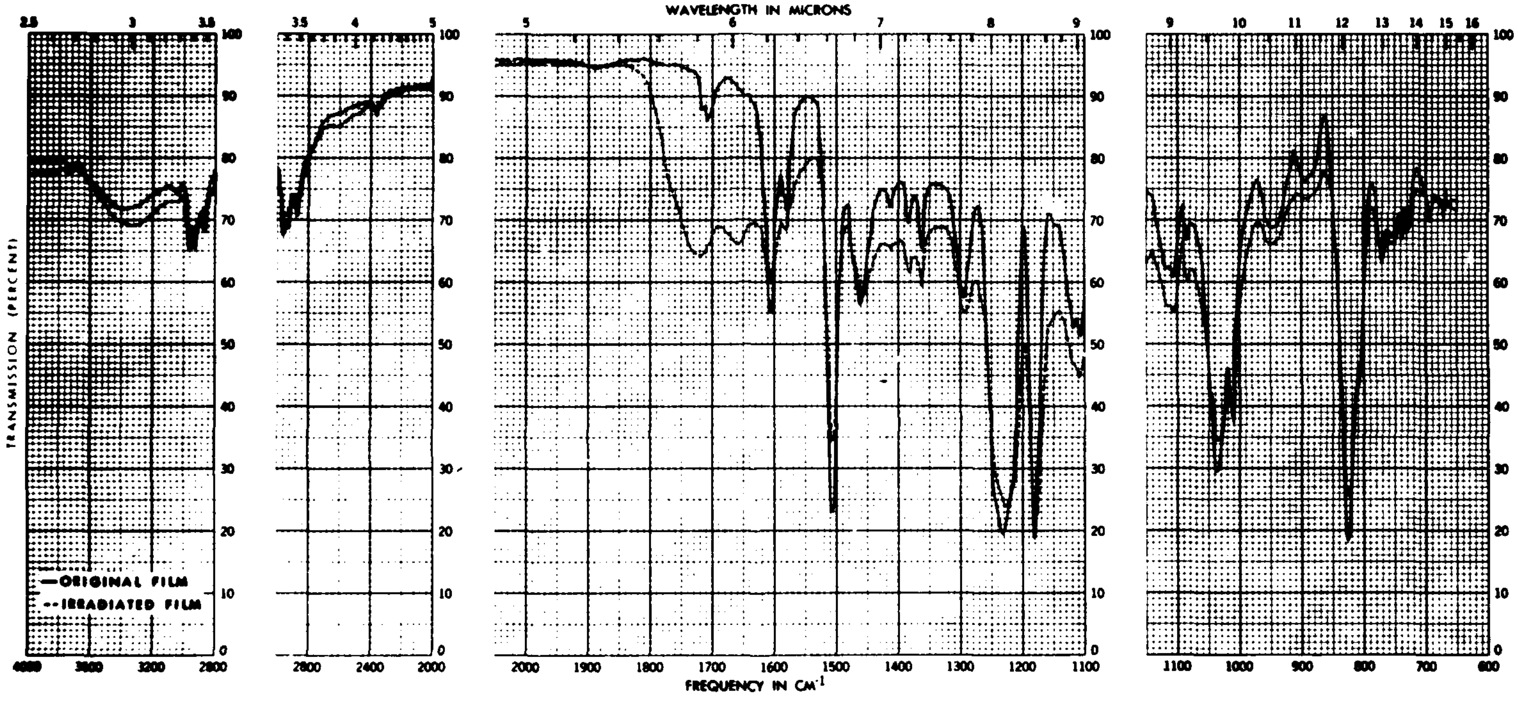

Figure 9. Effect of mercury-arc irradiation on the ATR spectrum of a clear epoxy-amine film.

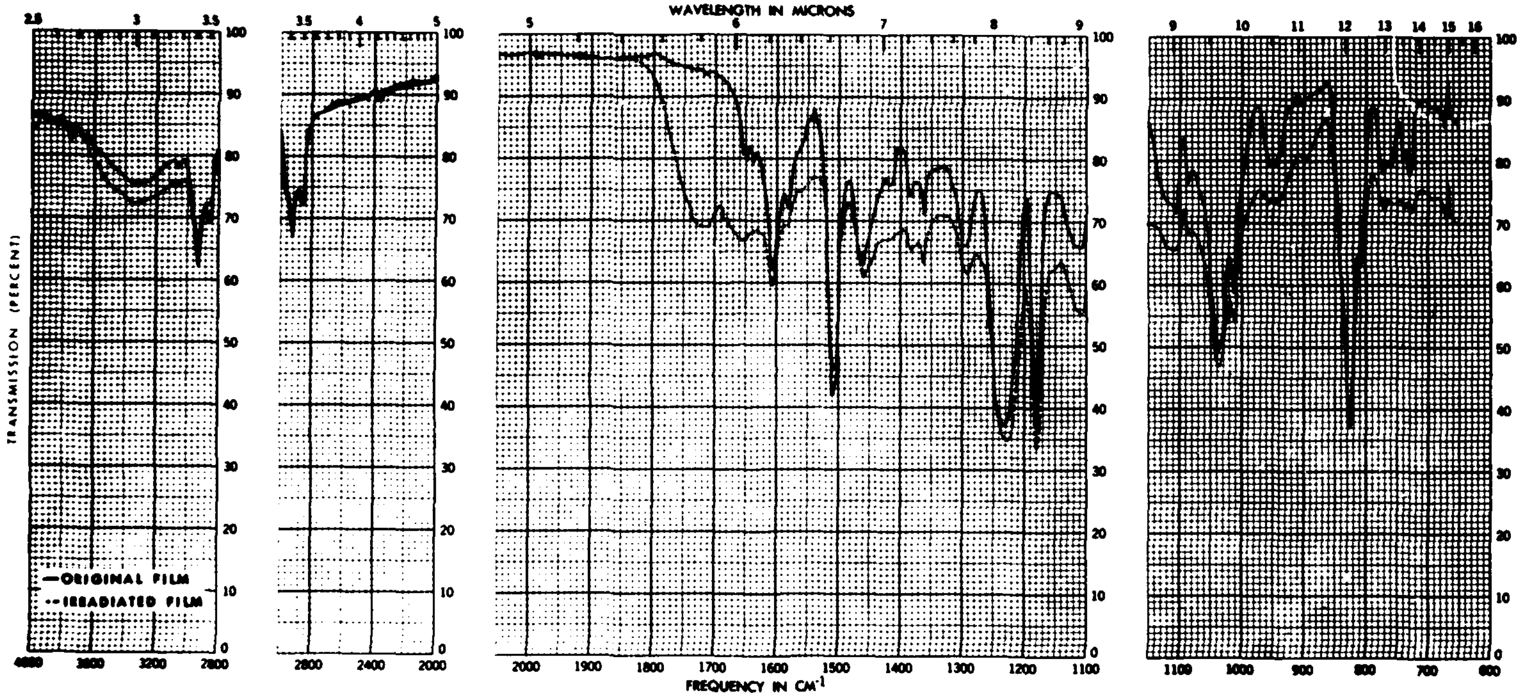

Figure 10. Effect of mercury-arc irradiation on the ATR spectrum of a clear epoxy-polymide film.

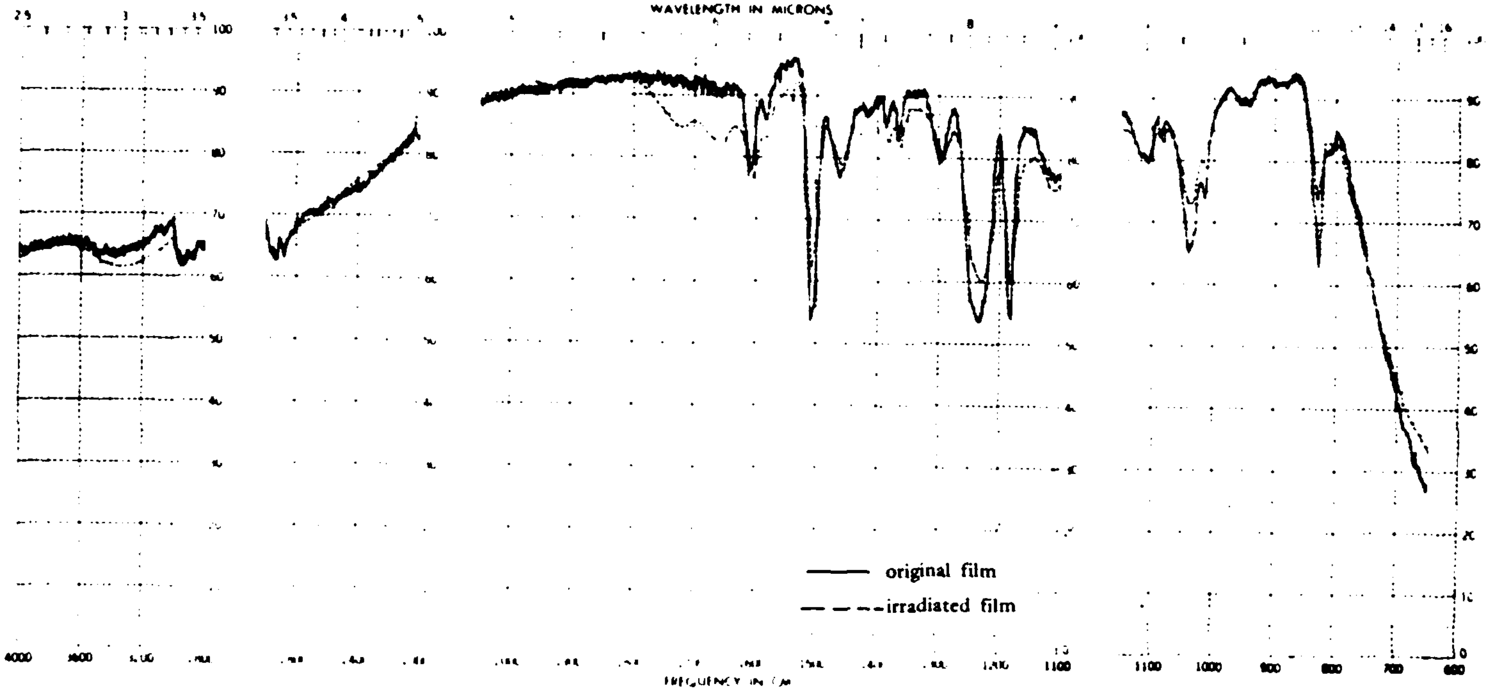

Figure 11. Effect of atmospheric exposure on the ATR spectrum of a pigmented amine-cured epoxy film.

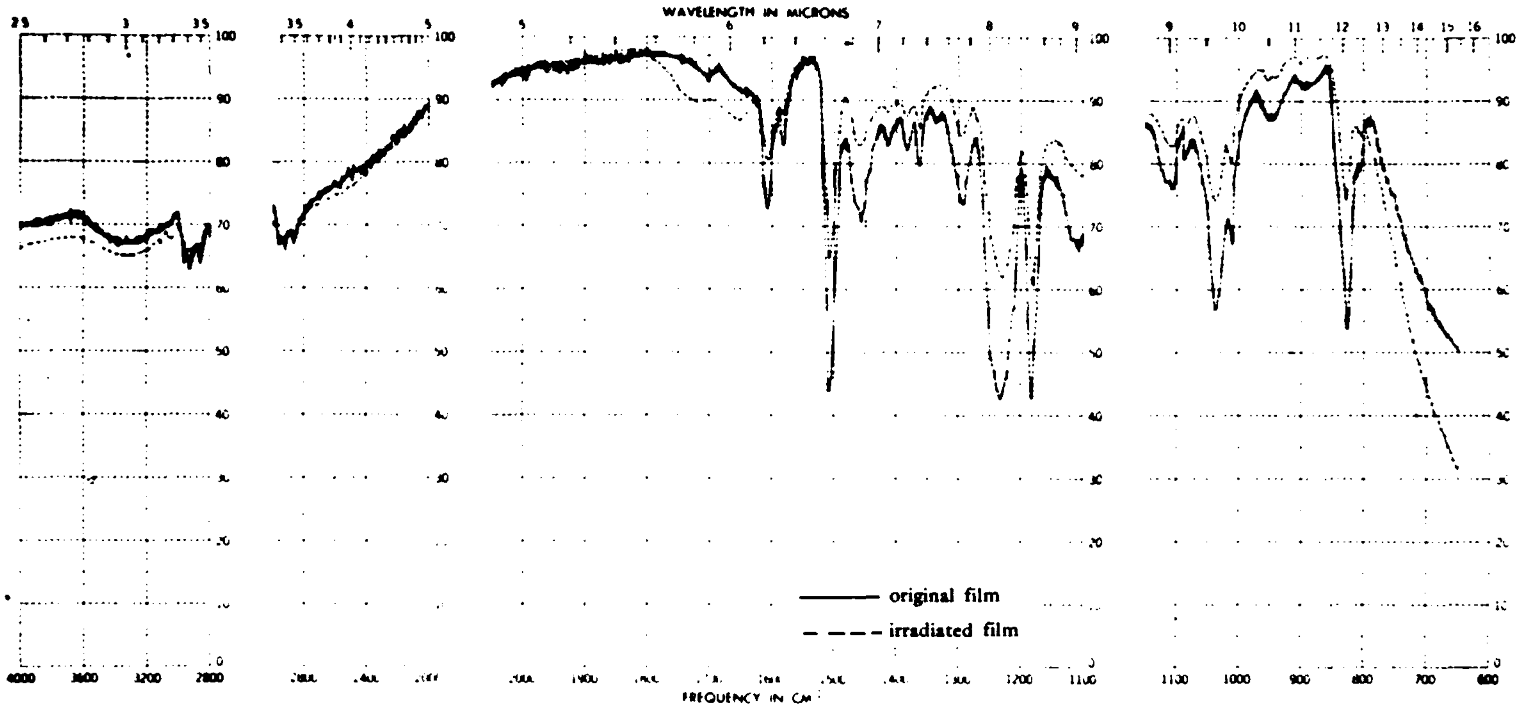

Figure 12. Effect of atmospheric exposure on the ATR spectrum of a pigmented, polyamide-cured epoxy film.

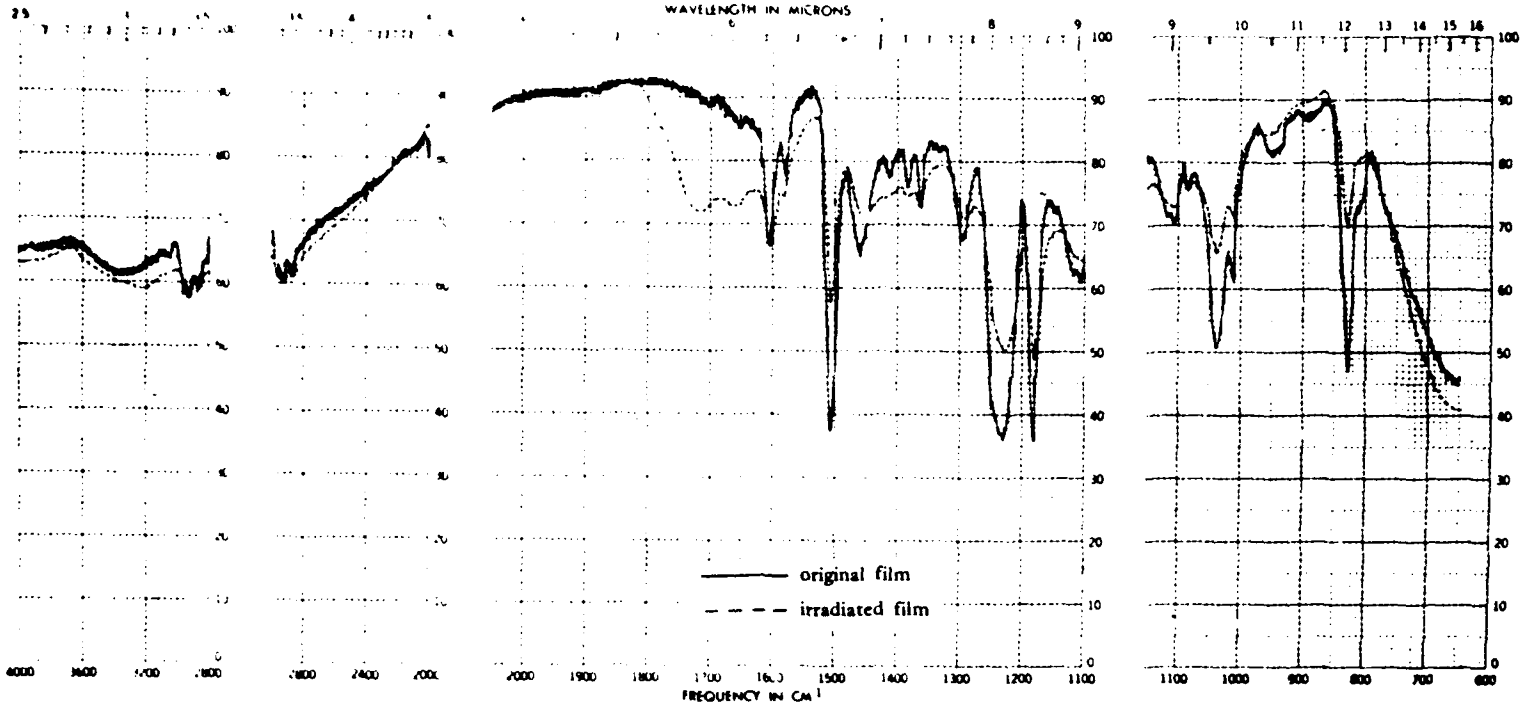

Figure 13. Effect of xenon-arc exposure on the ATR spectrum of a pigmented, polyamide-cured epoxy film.

The xenon-arc irradiations and the atmospheric exposures produced considerable effects on the ATR spectra of only the epoxy films. A slight increase in carbonyl absorption was also observed for the partially hydrolyzed vinyl film. These effects were all related to carbonyl absorption and were observed in coating films with relatively little initial carbonyl absorption.

Other investigators have recently studied the effect of weathering machines and outdoor exposures on the ATR spectra of plastics [8, 9]. For both polyethylenes and acrylonitrile-butadiene-styrene resins they found primarily the formation of carbonyl peaks at 1710 cm^{-1}. It thus appears likely that ATR spectroscopy will have its greatest usefulness in determining the surface effects of weathering of those coatings that do not have strong initial carbonyl absorption.

Photodegradation does produce measurable changes in the ATR spectra of organic coatings. The magnitude of these changes is sometimes small as compared to the potential experimental errors in the method. Without further investigations, it is not indicated that results of ATR measurements can be used in the prediction of coating performance.

CONCLUSIONS

1. The effects of atmospheric exposure on the surface of coating films, as detected by attenuated total reflectance (ATR) spectroscopy, are generally much more similar to those of xenon-arc irradiation than to those of mercury-arc irradiation.

2. Atmospheric exposure (a) produced slight decreases in the absorption peaks of alkyd and vinyl coatings, which showed little visual change; (b) produced a considerable decrease in the absorption peaks of an oil paint, which lost gloss and yellowed during the same exposure; and (c) produced slight decreases in the absorption peaks and an increase in carbonyl absorption in epoxy coatings, which lost gloss and yellowed. There was, therefore, a qualitative correlation between changes in ATR spectra and visual changes.

3. Long-term xenon-arc irradiation (500 hours) produced a negligible effect on the ATR spectrum of an alkyd coating, a slight effect on the spectrum of a vinyl film, and a strong effect, especially as compared to the effect of atmospheric exposure, on the spectrum of an epoxy film. Although xenon-arc irradiation more nearly approximates atmospheric exposure than mercury-arc irradiation, the relative effect of xenon-arc irradiation as compared to atmospheric exposure differs for various generic types of coatings.

4. The main effect of atmospheric exposure, as well as artificial irradiation, on the surface of organic coating films, as judged by the ATR spectra, is an increase in carbonyl content. This method of testing coatings, therefore, appears most suited for those synthetic coatings and plastics that do not have strong initial carbonyl absorption.

5. Although photodegradation produces measurable changes in the ATR spectra of organic coatings, no definite usefulness has been established for this method in the prediction of coating performance.

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