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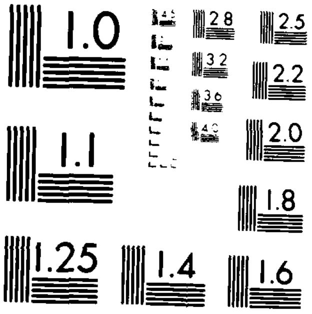

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ULTRAVIOLET CURABLE RESIN SYSTEM FOR RAPID RUNWAY REPAIR

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In this exploratory program, the UV-initiated cure of small test samples (2 inches by 2 inches by 3/4 inch) of a furan resin concrete was demonstrated. However, due to the high cost of the UV initiator (diphenyliodonium hexafluoroarsenate), the amount of initiator required to obtain complete cure results in a very high-cost polymer concrete. Three approaches -- reducing the (over)

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amount of initiator, use of a catalyst, and use of alternate, more reactive initiators -- for reducing the cost of the UV-initiated furan concrete were investigated. None of these approaches, all of which would effectively reduce cost through reducing the amount of required initiator, yielded a completely cured furan concrete upon UV exposure.

Therefore, although the concept of obtaining a highly controllable furan concrete through UV-initiated cure appears to be feasible (proven only for small-sized samples), the cost of the UV-curable system is too high to effectively compete with the other polymer concrete systems being considered in the Rapid Runway Repair Program.

PREFACE

This report was prepared by the Columbus Laboratories of the Battelle Memorial Institute, Columbus, Ohio, under Contract No. F08635-82-C-0214, for the Air Force Engineering and Services Center, Engineering and Services Laboratory (AFESC/RD), Tyndall Air Force Base, Florida.

This report summarizes work done between 15 March 1982 and 15 September 1982. Captain Daniel J. Pierre was the AFESC (RDCR) project officer.

This technical report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

1. BACKGROUND

In previous bomb damage repair work conducted by Battelle for the U. S. Air Force(Reference 1), furan and epoxy resins have shown potential as binders for polymer concrete which can be used to cap bomb craters in runways. Furan resin systems were formulated which satisfied the curing and flexural strength requirements over the wide range of required environmental conditions (-20°F, 70°F, and 105°F/wet and dry). An epoxy system was also formulated which satisfied all of the Air Force's requirements except for cure at low temperatures (-20°F). With -20°F aggregate and room-temperature resin, the epoxy did not cure in the required time.

The application of these resin systems involves the initial mixing of the resin with either a catalyst or promoter with reaction (hardening) occurring within approximately 5 minutes after mixing. As a result, there is very little working time after mixing. This problem of short working times is particularly pronounced with the furan resin which, in general, cures more rapidly than the epoxy. Also, for the furan resin system, a relatively high concentration of catalyst is required for low-temperature (-20°F) curing, which further increases the reaction rate and, thereby, limits controllability.

2. OBJECTIVE

The principal objective of this exploratory research program was the development of an ultraviolet (UV)-initiated curing mechanism for furan and epoxy resin-based polymer concrete structural caps. In practice, the resin concrete system may remain workable up until the time curing with a UV light source is initiated.

3. CONCEPT

To accomplish the objective, a latent catalyst system is required which, when exposed to UV light, produces reactive species which cure epoxy and furan resins. To be practical with respect to large crater repair, the curing reactions should continue when the UV source is removed. In this way, a compact UV light source could be used to initiate curing at various points around a polymer concrete cap, and the long-time exposure of the entire cap would not be required.

a. Potential UV Initiator System

Based on the above requirements for a UV-initiated latent catalyst system, conventional UV initiator systems cannot be used, since with these systems, the initiation process (and polymerization process) stops upon UV light removal. Also, with conventional UV initiator systems, only polymer films of mil thicknesses have been cured. However, if the polymerization process continues when the UV light source is removed, it may be possible to cure thick slabs of polymer. For crater repair, the applicability of such a system would depend upon the rate of cure after removal of the UV light source.

Upon exposure to UV light, diaryliodonium salts ($AR_2I^+MX_n^-$) produce a strong acid ($MX_n^-H^+$) which can catalyze furan resin polymerization and cationically initiate epoxy resin polymerization (see Figure 1). The chemical properties of the anionic portion of the acid (MX_n^-) allow for continued epoxy resin polymerization following light removal, and the high reactivity of furan resins (and furfuryl alcohol) should also provide for continued furan resin polymerization after removal of the initiating UV light. Therefore, the diaryliodonium salts appear to be very viable UV initiator systems for epoxy and furan polymer concrete caps.

b. Choice of Diaryliodonium Salts Over Other Similar UV Initiators

In comparison to diaryliodonium and alklaryliodonium salts (other potential iodonium salt initiator systems), the diaryliodonium salts are considerably more stable and are readily isolated and purified by conventional techniques. In addition, the diaryliodonium salts are stable in the absence of UV light and in the presence of highly reactive resin systems (possibility of storing initiator system in resin). Also, pertinent information with respect to synthesis procedures, photochemistry, and photoinitiation capabilities is well documented in the literature for the diaryliodonium salts.

$$Ar_2I^+MX_n^- \xrightarrow{UV} [Ar_2I^+MX_n^-]^*$$

$$[Ar_2I^+MX_n^-]^* \longrightarrow Ar\text{-}I\cdot^+ + Ar\cdot + \boxed{MX_n^-}$$

$$Ar - I\cdot^+ + SH \longrightarrow Ar - IH^+ + S\cdot$$

$$Ar - IH^+ \longrightarrow Ar - I + \boxed{H^+}$$

$$\begin{tikzcd} & \text{Furan Polymerization} \\ MX_n^-H^+ \arrow[ur] \arrow[dr] & \\ & \text{Epoxy Polymerization} \end{tikzcd}$$

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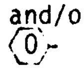
* = Excited State Species
• = An Electron
SH = Solvent and/or Resin
Ar = Aryl ()

Figure 1. Diaryliodonium Salt Decomposition upon UV Exposure

Tiarylsulfonium salts react in the same manner as diaryliodonium salts upon UV exposure. A diaryliodonium salt was chosen over a triarylsulfonium salt for the initial experiments in this program since diaryliodonium salts have been reported as being slightly more UV-reactive than triarylsulfonium salts(Reference 2) and sensitizers* are more effective with diaryliodonium salts than with triarylsulfonium salts(Reference 3).

c. Disadvantages of Diaryliodonium Salts

Iodonium salts, in general, are not commercially available. The cost of diphenyl iodonium hexafluoroarsenate, the principal diaryliodonium salt used in this study, is approximately $2,329 per pound based solely upon the cost of the ingredients used in its synthesis. Depending on the concentration of the iodonium salt required for adequate cure (adequate flexural strength in the required time), the cost of a UV-initiated furan or epoxy polymer concrete cap could be greatly increased in comparison to the conventionally cured cap.

d. Choice of Diphenyliodonium Hexafluoroarsenate Salts (DPIHAs) as Latent Catalyst

DPIHAs is a specific example of the general classification of onium salts designated diaryliodonium. The reason for choosing DPIHAs the primary UV initiator is discussed in the following paragraphs.

In the interaction of an oniom salt (such as $Ar_2I^+MX_n^-$) with UV light, the anionic portion (MX_6^-) remains unchanged and appears in the products as the acid $H^+MX_n^-$ which initiates polymerization. The most common anions are $BF_4^-PF_6^-$, AsF_6^-, and SbF_6^-. Crivello and Lam(Reference 4) have shown that the nature of the anion does not play a role in determining the UV sensitivity of an iodonium salt. This suggests that the amount-per-unit times of different acids generated by iodonium salts containing the same cation but different anions are identical. However, the nature of the anion is important with respect to the ability of the acid which is generated ($H^+PF_6^-$, $H^+AsF_6^-$, $H^+SbF_6^-$) to initiate polymerization. Based on the photoinitiated (UV-initiated) polymerization of various monomer types using diaryliodonium and triarylsulfonium salts containing PF_6^-, AsF_6^-, SbF_6^-, and BF_6^- anions, Crivello and Lam (Reference 4) have reported the order of reactivity (in terms of rate of polymerization) of the acids generated as $H^+SbF_6^- > H^+AsF_6^- > H^+PF_6^- > H^+BF_6^-$ (most reactive to least reactive). This order of reactivity has also been observed in other instances not involving photoinitiated polymerization and was explained on the basis of the strength of the ionic bond between the anion and H^+ (Reference 5). The larger the negatively charged ion, the more loosely it is bound to the cation, and the more active the cation in polymerization. In the above order of reactivity, the size of the anion decreases in the same direction as the decrease in reactivity.

Although $H^+SbF_6^-$ (Sb = Antimony) is more reactive than $H^+AsF_6^-$ (As = Arsenic), DPIHAs was chosen for the initial experiments of this program. This choice was predominantly based on the fact that a study has been made on the effect of sensitizers in enhancing the UV reactivity of DPIHAs(Reference 3). The importance of using sensitizers will be discussed under "UV Wavelength Considerations."

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* The definition of sensitizer and the role of sensitizers in this program will be presented under "UV Wavelength Considerations," page 5.

e. UV Wavelength Considerations

There are two principal considerations. First, the diaryliodonium salt must absorb UV light to function as a photoinitiator. As a result, the salt must absorb strongly in a wavelength region where the resin has low absorption. Second, for efficiency of light utilization, the salt should absorb strongly at 313 millimicrons (mμ) (1 millimicron = 10 angstroms = 1×10^{-10} meter) and 366 mμ which are the wavelengths of maximum output intensity for medium- and high-pressure mercury vapor UV lamps.

Diaryliodonium salts show very low absorptivity in the 300 to 400 mμ spectral region where UV lamps generally supply substantial emission. This problem can be overcome through the use of sensitizers which strongly absorb in the 300 to 400 mμ region. In practice, the sensitizer then interacts with the iodonium salt to produce the same products as those produced upon photodecomposition of the iodonium salt in the absence of a sensitizer.

Pappas and Jilek (Reference 3) have investigated the abilities of various sensitizers to reduce the time required for diphenyliodonium triphenylsulfonium hexafluoroarsenate to gel (polymerize) a diepoxide upon exposure to 366 mμ UV light. Every sensitizer studied was effective in substantially reducing gelation time in combination with the diphenyliodonium salt but not with the triphenylsulfonium salt. Thioxanthone was found to be the most effective sensitizer for the diphenyliodonium salt. It reduced the gel time from approximately 85 minutes to 7 minutes, and, as a result, was chosen for use in the initial experiments in this program.

Therefore, DPIHAs, alone or in combination with thioxanthone, were chosen as the primary initiator candidates for the UV-initiated cure of epoxy or furan-based polymer concrete.

4. RESEARCH APPROACH

Because of the need to identify candidate furan and epoxy prepolymers and the multiple-screening requirements (prepolymers and UV initiators), the research program was conveniently divided into two tasks provided for close technical management of the laboratory efforts.

In Task 1, the primary UV initiator candidate, DPIHAs was synthesized and several commercially available resin candidates were chosen. These resin candidates appear in Table 1 and were chosen based on their suspected high reactivity. It was expected that high resin cure rate (high exotherm) would be required to obtain complete cure after UV initiation of resin polymerization. Initiation of polymerization would presumably occur predominantly in a layer near the surface of the polymer concrete.

As discussed earlier, a resin system is susceptible to UV-initiated cure only if it has low UV absorption (window) in wavelength regions where the initiator salt, DPIHAs, or the potential sensitizer, thioxanthone, absorbs strongly. As a result, UV spectra of DPIHAs, thioxanthone, and the resin candidates were obtained in Task 1.

In Task 2, screening experiments were conducted to demonstrate the feasibility of the UV-initiated cure concept. In the initial experiments of Task 2, the resin systems which exhibited a UV wavelength window in the region where the iodonium salt strongly absorbs were combined with DPIHAs and screened for UV-initiated cure. Based on the results of these initial experiments, it became necessary to perform further screening experiments to demonstrate the ability to obtain complete cure and an economically acceptable UV-cured polymer concrete. The nature of these additional screening experiments is given in a detailed flow diagram of the research approach which appears in Figure 2. A detailed description of the experimental conditions and procedures used in Task 1 and 2 is presented in the next section.

TABLE 1. RESINS FOR WHICH UV SPECTRA WERE OBTAINED

Resin	Chemical Type	Manufacturer
Epon® 828 + Heloxy® 69*	Epoxy	Epon 828 - Shell Heloxy 69 - Wilmington Chemical Corporation
Chem Rez® 200	Furan	Ashland Chemical Company
Chem Rez® 201	Furan	Ashland Chemical Company
Chem Rez® 280	Furan	Ashland Chemical Company
Acme® 931	Furan	Acme Resin Corporation
Airkure® 06-00	Furan	Delta Resins
Airkure® 06-22	Furan	Delta Resins
Airkure® 06-612	Furan	Delta Resins
Furfuryl® alcohol	Furan	Quaker Oats
Corelube® CL1-1000	Furan	Corelube Santec

* Primary epoxy resin candidate from the previous bomb damage repair program conducted at Battelle(Reference 1).

5. EXPERIMENTAL

a. Materials

The UV initiators (diphenyliodonium hexafluoroarsenate, 4,4'-ditert-butyldiphenyliodonium hexafluoroantimonate and triphenylsulfonium hexafluoroarsenate) were prepared according to the methods of Crivello and Lam(Reference 6). Reasons for synthesizing 4,4-di-tert-butyldiphenyliodonium hexafluoroantimonate and triphenylsultonium hexafluoroarsenate in addition to DPIHAs will be discussed in Section II.2.e. The thioxanthone (sensitizer), furan resins, and epoxy resins were used as received from the manufacturer.

b. UV Spectra

Ultraviolet spectra were obtained using a Cary 14 Spectrophotometer. All spectra were of solutions using ethanol or acetonitrile as the solvents, and the concentration of each solution was 5×10^{-5}g/1000 ml.

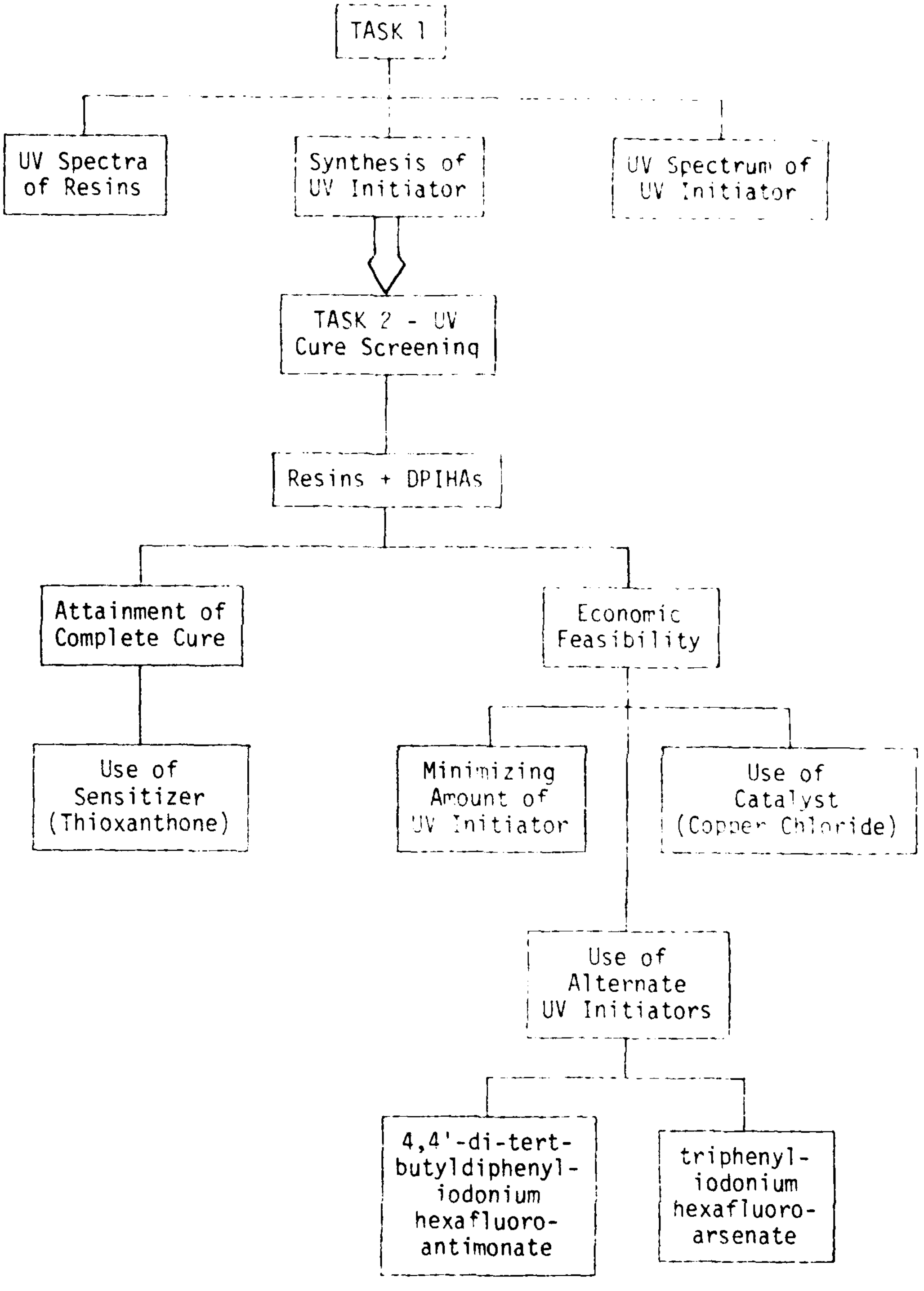

Figure 2. Flow Diagram of Research Approach

c. Preparation of Polymer Concrete Samples for UV Cure Screening Experiments

The resins were mixed with Parry quartz aggregate (1/4 inch by 1/8 inch) at a ratio of 70 parts aggregate to 30 parts resin by weight. The DPIHAs and thioxanthone were added to the resins initially as dry powders and, in later experiments, as a solution in acetone (all materials at room temperature). When added as a dry powder, the DPIHAs readily dissolved in the resins. Some of the thioxanthone, however, remained undissolved after extended mixing. The low solubility of thioxanthone in the resins was one reason for adding the initiator and sensitizer as a solution (in acetone) in later experiments. The use of a solution will be discussed further in Section II - Research Results.

d. UV Cure Screening Experiments

The polymer concrete samples (2 inches by 2 inches by 3/4 inch) were exposed to a 100-watt per inch Hanovia medium pressure (mercury vapor) ultraviolet lamp for 20 minutes. After exposure, the samples were qualitatively analyzed for cure and were observed for post-irradiation cure.

During the 20-minute exposure time, the cure chamber housing* heated up to approximately 110°F. To ensure that any observed cure was due to UV energy and not due to heat energy, samples identical to those exposed to UV were placed in an oven at 110°F for 30 minutes. Also, control samples which did not contain the iodonium salt or sensitizer were exposed to UV light.

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* For protection against eye exposure to UV light, a chamber was built for housing the UV lamp. To minimize heat buildup during operation of the lamp, an air stream was maintained through the chamber.

SECTION II

RESEARCH RESULTS

1. TASK 1 - UV SPECTRA OF RESINS AND INITIATOR/SYNTHESIS OF INITIATOR

Following the method of Crivello and Lam(Reference 6), the synthesis of DPIHAs was straightforward and no problems were encountered. A 48-percent yield was obtained and the solid product was recrystallized once from isoproanol. A melting point of 124°C was obtained for the white granular crystals. Crivello and Lam reported a melting point of 123° to 125°C.

Four of the furan resins (Airkure® 06-00, Airkure® 06-612, Airkure® 06-22 and Quaker Oats furfuryl alcohol) and the primary epoxy resin candidate from the previous BDR program (2 parts Epon 828 + 1 part Heloxy 69) were found to have acceptably low UV absorbances in a wavelength region between approximately 240 mμ and 260 mμ, where the DPIHAs strongly absorbs. A comparison of the UV spectrum of DPIHAs with UV spectra of two of the resin candidates exhibiting acceptable absorbance windows is given in Figure 3.

Ultraviolet spectra of the candidate resins and DPIHAs appear in Appendix B. These spectra are of solutions in ethanol or acetonitrile. These solutions were equal in concentration containing 5 x 10^{-5} grams of DPIHAs or resin in 1000 milliliters of solvent.

Since in actual application the concentration of resin will be much greater than the concentration of DPIHAs, it is important that at equal concentrations (g/1000 ml) the absorbance of DPIHAs is considerably greater than the absorbance of the resin in the 240-260 mμ region. At application concentrations this large difference in absorbance at equal concentrations is needed for DPIHAs to effectively compete with the resin for absorption of the incident 240-260 mμ light. As reviewed in Appendix A, absorbance of UV light by a compound in a solution is directly proportional to the concentrations of that compound. Therefore, the larger the difference between UV absorbance of DPIHAs and the resin in the 240-260 mμ region, a larger concentration difference between DPIHAs and the resin can be tolerated before DPIHAs no longer absorbs sufficient UV light to initiate resin cure. Calculations describing this concept of competitive light absorption are provided in Appendix A. Also, since the amount of cure-initiating species (H^+) produced is directly proportional to the amount of UV light absorbed by DPIHAs, the amount of UV light absorption by DPIHAs required to initiate cure and obtain complete cure will presumably be lower for highly reactive resins.

Therefore, based on their suspected high reactivity and their very low absorbances in the 240 mμ - 260 mμ wavelength region (compared to DPIHAs at equal concentrations) Airkure® 06-00, Airkure® 06-612, Airkure® 06-22, Quaker Oats furfuryl alcohol and the epoxy resin appear to be viable candidates for combination with DPIHAs to potentially provide a UV-initiated polymer concrete.

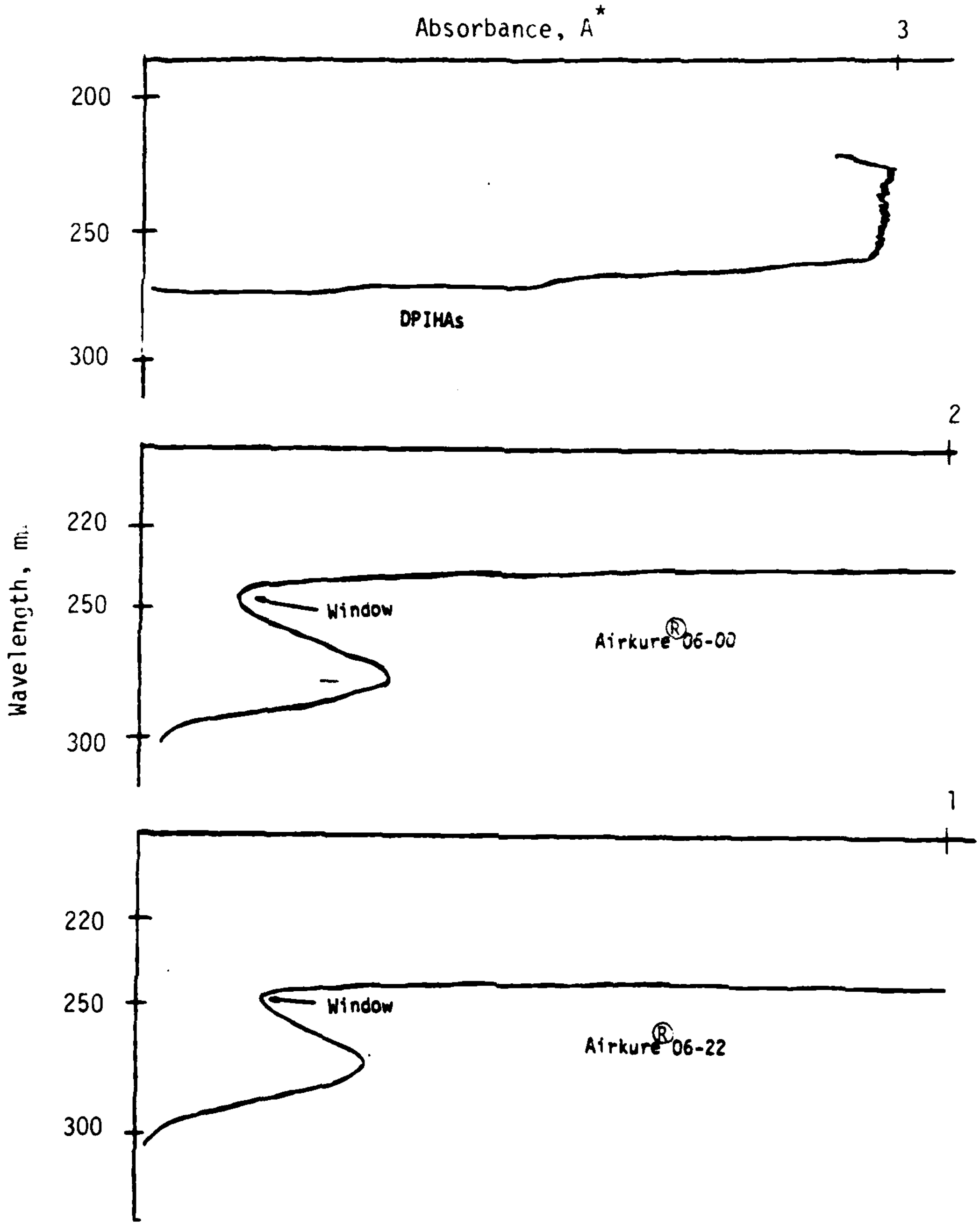

Figure 3. UV Spectra of DPIHAs, Airkure® 06-00 and Airkure® 06-22

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* Definition of A given in Appendix A.

2. TASK 2 - LABORATORY SCREENING

a. Initial Screening Experiments - Resin + DPIHAs

The initial resins screened in this program were Airkure® 06-00 and 06-612 (furan resins) and the primary epoxy candidate from the previous BDR program (Epon® 828 + Heloxy®). Exposure of these resins (mixed with aggregate) containing 10 percent by weight of DPIHAs (based on resin) to the UV light source for 20 minutes results in only surface cures of the furans; the epoxy did cure to approximately one-half the depth of the sample.

b. Use of Sensitizer to Obtain Complete Cure

In an attempt to obtain complete (through) cure, a sensitizer, thioxanthone, was added as part of the initiator system. Based on the following observations, the addition of thioxanthone should result in the formation of a higher concentration of cure-initiating species (H^+).

1. The iodonium salt has low absorption in the wavelength region of highest output intensity of the UV lamp (300 to 400 mμ).
2. The resins have low absorption in the 300 to 400 mμ region.
3. Thioxanthone (UV spectrum in Appendix B) absorbs strongly in the 300 to 400 mμ region.

Presumably, the thioxanthone will absorb UV light in the 300 to 400 mμ region. The excited state thioxanthone then interacts with DPIHAs to produce the same cure-initiating species as would result from the UV decomposition of DPIHAs but at a higher concentration because of more efficient utilization of the available UV light.

Using 10 percent DPIHAs and 2 percent thioxanthone (5 percent in the case of Airkure® 06-612 -- error in weighing), the same cure results (20-minute exposure to UV lamp) were obtained as in the absence of thioxanthone with the exception of the Airkure® 06-00 which did cure throughout. These results are summarized in Table 2. The Airkure® 06-00 control (containing 10 percent DPIHAs and 2 percent thioxanthone) which was placed in a 110°F oven for 30 minutes (no UV light) did not show signs of cure initiation. Therefore, the through-cure of the Airkure® 06-00 system upon exposure to the UV light was not due entirely to the heat generated by the UV lamp.

The attainment of a UV-initiated cure to a depth of 3/4 inch is an encouraging result. However, the use of 10 percent iodonium salt by weight will result in a very expensive polymer concrete structural cap. The choice of 10 percent by weight as the required amount of DPIHAs was based on the fairly large amounts of onium salt (iodonium and sulfonium) used in the literature to UV-cure thin (1- to 2-mil) coating films(Reference 7) and on calculations (see Appendix A) which indicated that a least 10percent DPIHAs was required to effectively compete with Airkure® 06-00 for absorption of 240-260 mμ UV light.

TABLE 2. INITIAL UV CURE RESULTS

Resin	Percent by Weight[a] DPIHAs (UV Initiator)	Percent by Weight[a] Thioxanthone (Sensitizer)	Cure Results (20-Minute Exposure to UV Lamp)
Airkure® 06-00	10	0	Surface cure only
Airkure® 06-00	10	2	COMPLETE CURE
Airkure® 06-612	10	0	Surface cure only
Airkure® 06-612	10	5	Surface cure only
Epoxy	10	0	Cured to 1/2 depth of sample
Epoxy	10	2	Cured to 1/2 depth of sample
Airkure® 06-00 (Control)	0	0	No cure

(a) Based on resin.

Therefore, instead of forming large beams of the Airkure® 06-00/DPIHAs system, research efforts were directed toward approaches for substantially lowering the cost of the UV-initiated furan concrete. These approaches are discussed in the following paragraphs.

c. Minimizing the Amount of DPIHAs to Reduce Cost

The following approach was then used to try to overcome the high cost problem. Since only the UV light absorption of the thioxanthone in the 300 to 400 mμ region is of interest and since the thioxanthone and iodonium salt interact in a 1:1 stoichiometry to produce the initiating species(Reference 2), the amounts of thioxanthone and DPIHAs added to the resins were reduced to 0.05 percent and 0.1 percent, respectively (by weight based on resin). These amounts of thioxanthone and DPIHAs represent a 1:1 molar stoichiometry, and based on Beer's Law*, 0.05 percent of thioxanthone is sufficient to absorb greater than 99 percent of the incident 313 and 366 mμ UV light (wavelengths of maximum output by the lamp) in a path length of 2 cm (3/4 inch) through the polymer concrete samples. This assumes very low UV absorption in the 300-400 mμ region by DPIHAs and Airkure® 06-00 which, based on their UV spectra, is a good assumption. Also, to more thoroughly disperse the DPIHAs and thioxanthone throughout the resins, they were first dissolved in acetone (1 ml) and then added to the resins. The acetone does not absorb in the 300 to 400 mμ region and does not interfere with the overall initiation reaction.

The results are summarized in the first three rows of Table 3. In addition to the resins initially investigated, Airkure® 06-22 and furfuryl alcohol (Quaker Oats) were also screened for UV-initiated cure (20-minute UV exposure). None of the resins cured completely. In fact, only two of the resins, Airkure® 06-00 and the epoxy, exhibited visual signs of some degree of cure. The epoxy gave a hard surface cure with the center of the sample remaining liquid. The same overall results were obtained upon doubling and tripling the thioxanthone and DPIHAs concentrations. Also, the attainment of cure upon standing (after UV exposure) was not observed for any of the above samples.

Therefore, concentrations greater than 0.15 percent thioxanthone and 0.3 percent DPIHAs are required to obtain through-cure of Airkure® 06-00 which appears to be the resin of interest. Airkure® 06-612, Airkure® 06-22 and furfuryl alcohol do not appear to be susceptible to UV-initiated cure using cost-effective amounts of thioxanthone and DPIHAs. The cure of the epoxy resin system is initiated but complete cure is not obtained. Also, none of the resin systems exhibited complete cure upon prolonged standing after UV exposure.

In an attempt to determine to what extent the DPIHAs concentration could be lowered, 3 percent iodonium salt/2 percent thioxanthone (based on resin weight) was added to Airkure® 06-00. After 20 minutes of UV exposure, the resin had darkened throughout, with some surface cure. Also, complete cure was not obtained upon standing.

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* Beer's Law is described in Appendix A.

TABLE 3. UV CURE RESULTS FOR REDUCED AMOUNT OF INITIATOR

		Airkure® 06-00	Airkure® 06-612	Airkure® 06-22	Furfuryl Alcohol (Quaker Oats)	Epoxy
0.10% DPIHAs 0.05% TXT(b)	UV(a)	Cure initiated, resin darkened on surface	No cure	No cure	No cure	Hard surface only
	Oven(c)	No cure	No cure	No cure	No cure	No cure
0.20% DPIHAs 0.10% TXT	UV	Cure initiated, resin darkened on surface	No cure	No cure	No cure	Hard surface cure only
	Oven	No cure	No cure	No cure	No cure	No cure
0.30% DPIHAs 0.15% TXT	UV	Cure initiated, resin slightly darkened throughout	No cure	No cure	No cure	Hard surface cure only
	Oven	No cure	No cure	No cure	No cure	No cure
0.20% CuCl, 0.10% DPIHAs 0.05% TXT	UV	Cure initiated, resin darkened throughout	No cure	No cure	No cure	Hard surface cure only
	Oven	No cure	No cure	No cure	No cure	No cure
1% CuCl	UV	Cure initiated, resin darkened and increased in viscosity	No cure	No cure	No cure	No cure
	Oven	No cure	No cure	No cure	No cure	No cure
Control - No DPIHAs, TXT, or CuCl	UV	No cure	No cure	No cure	No cure	No cure
	Oven	No cure	No cure	No cure	No cure	Not tested

(a) UV exposure, 20 minutes.

(b) Thioxanthone.

(c) 110 F oven exposure, 30 minutes.

Therefore, a concentration of DPIHAs greater than 3 percent is required. This results in a very expensive UV-initiated polymer concrete structural cap. However, if the iodonium salt and thioxanthone did not have to be present throughout the polymer concrete and could initiate complete cure as a thin layer (resin + UV initiator system) on the surface of the cap, then cost would be reduced to an acceptable level. Pursuing this idea, just prior to UV exposure Airkure® 06-00 containing 20 percent DPHIAs and 4 percent thioxanthone was poured onto Airkure® 06-00/aggregate, forming a thin layer on the surface of the bar sample. Upon 20 minutes of UV exposure, the resin darkened but complete cure was not obtained. Evidently, the concentrate was rapidly diluted by diffusion throughout the sample.

d. Use of a Catalyst to Reduce Cost

Since it can act as a latent catalyst for the cure of furan resins, and can also catalyze the DPIHAs/thioxanthone UV initiation process, cupric chloride was screened as a catalyst for the UV-initiated cure (data appear in Table 3). If cupric chloride does act as a catalyst, the low concentrations of thioxanthone and iodonium salt screened above may be sufficient to give complete cure. The potential of cupric chloride to act as an active or latent catalyst for the Airkure® 06-00/DPIHAs/thioxanthone system will be discussed in the following paragraphs.

Copper compounds (organic and inorganic salts) have been used as catalysts for oxidation/reduction reactions involving diaryliodonium salts(Reference 8). The mechanism for UV initiation of polymerization (through formation of MX^-H^+) by the iodonium salt and sensitizer system has been proposed as involving an electron transfer or oxidation/reduction step(Reference 3). Therefore, cupric chloride may be an active catalyst for the UV initiation of polymerization.

A recent BDR program conducted by Battelle for the Air Force Engineering and Services Center (Contract F08635-82-C-0187, Heat-Initiated Furan Resin for Rapid Runway Repair), demonstrated that cupric chloride acts as a latent catalyst to initiate the cure of a furan resin-based concrete upon localized heating. Therefore, in addition to having the potential of being an active catalyst for the DPIHAs/thioxanthone UV initiation process, the cupric chloride may also act as a latent catalyst which can enhance cure. Recall that Airkure® 06-00 containing 0.05 percent thioxanthone and 0.1 percent DPIHAs did darken upon UV exposure. Presumably, any localized exotherm resulting from this indicated small degree of cure may trigger the cupric chloride.

The addition of 0.2 percent cupric chloride to the Airkure® 06-00/DPIHAs (0.1 percent)/thioxanthone (0.05 percent) system did not improve cure upon UV exposure. The use of larger amounts of DPIHAs and thioxanthone (greater potential for heat buildup) with the cupric chloride was not investigated. The object is to reduce, not increase, the amounts of these compounds. Also, the reason for not using larger percentages of cupric chloride will become evident in the following paragraphs.

An interesting result was obtained when, as a control, the UV-initiated cure of Airkure® 06-00 (plus aggregate) in the presence of cupric chloride (1 percent) alone was tested. Cure was initiated as shown by a darkening and appreciable increase in viscosity of the resin. However, the Airkure® 06-00/cupric chloride combination also darkened when placed in a 110°F oven for 30 minutes, but it did not undergo an observable increase in viscosity.

Therefore, it appears that the apparent UV activity of cupric chloride is caused, at least in part, by the heat generated by the UV lamp. In fact, when cupric chloride/Airkure® 06-00 systems which contained amounts of copper chloride in excess of 1 percent were exposed to the UV lamp, it became apparent that any indication of cure initiation was principally due to heat. Upon UV exposure, the samples began darkening at the bottom of the bar sample rather than at the top as would be expected if UV light were responsible for cure initiation. These data are in accordance with the demonstrated ability of cupric chloride to act as a heat-triggered latent catalyst for furan concrete.

The ability of other organic or inorganic copper salts to catalyze the UV initiation process was not investigated. Instead, research efforts were directed toward the use of alternate, more reactive, UV initiator salts.

e. Use of Alternate UV Initiator Salts

Since it appears that greater than 3 percent of DPIHAs is required for complete cure of the principal resin candidate, Airkure® 06-00, a UV-initiated polymer concrete based on DPIHAs is economically unfeasible.

However, the possibility that economically acceptable amounts of other similar UV initiator salts may be able to completely cure Airkure® 06-00 was investigated. Two salts, triphenylsulfonium hexafluoroarsenate and 4,4'-Di-tert-butyldiphenyliodonium hexafluoroantimonate were chosen for investigation. The reasons for choosing these two UV initiator salts and their applicability as UV initiators for Airkure® 06-00 will be discussed in the following subsections.

(1) 4,4'-Di-tert-butyldiphenyliodonium Hexafluoroantimonate

The acid H^+SbF_6 (Sb = Antimony) has been shown to be much more reactive than H^+AsF_6 (As = Arsenic) in the initiation of polymerization (discussed on page 3 of this report). In fact, the UV initiation of epoxy polymerization using iodonium and sulfonium hexafluoroantimonate has been reported to result in very rapid and exothermic polymerizations (References 4 and 9). Based on this, it may be possible to use much smaller amounts of a diaryliodonium hexafluoroantimonate salt than the corresponding arsenate salt to obtain the complete cure of Airkure® 06-00. Also, the antimonate salts are somewhat less expensive than the arsenate salts.

Initially, an attempt was made to synthesize diphenyliondonium hexafluoroantimonate (DPIHAt). However, because the DPIHAt is very unstable (readily hydrolyzes), it was never successfully separated from the reaction mixture.

The synthesis of 4,4'-d-tert-butyldiphenyliodonium hexafluoroantimonate (DTBPIHAt) was then attempted since it has been reported to be more hydrolytically stable than DPIHAt. The solid DTBPIHAt was successfully separated from the reaction mixture. However, the melting point obtained for the product was not within the range of that reported in the literature. Presumably, hydrolyzation was slowly occurring upon standing. Because of this instability, the use of DTBPIHAt was considered impractical

(2) Triphenylsulfonium Hexafluoroarsenate

The literature conflicts as to the ability of triarylsufonium salts to UV initiate polymerization of epoxy systems. Some researchers report rapid reaction times; others report very slow reaction times. Based on the possibility of rapid reaction times (small, economic amount of initiator required) and on the reported long-time storage stability of the triarylsulfonium salts in combination with resin systems (Reference 7) (possibility of storing UV initiator and resin together), triphenylsulfonium hexafluoroarsenate (TPSHAs) was synthesized and screened as a UV initiator for the cure of Airkure® 06-00.

The synthesis of TPSHAs was straightforward. A 60-percent yield of a white granular crystalline solid was obtained. The TPSHAs was recrystallized from ethanol and a melting point of 195°C was obtained. A melting point of 194° to 197°C is reported in the literature.

The TPSHAs, alone and in combination with a sensitizer, did not initiate the cure of Airkure® 06-00 upon UV exposure (see Table 4). To reduce the number of UV cure screening experiments, a large amount of TPSHAs was initially tested. If cure was not obtained (as it was not) with this economically unacceptable amount of TPSHAs, then further experiments would not be necessary.

Anthracene was used as the sensitizer in place of thioxanthone. In the sensitization of TPSHAs, anthracene has been reported (Reference 3) to be more effective than thioxanthone. Both the anthracene and TPSHAs were added to the Airkure® 06-00 as solids. No solubility problems were encountered.

TABLE 4. UV CURE RESULTS FOR TPSHAs/AIRKURE® 06-00

Percent TPSHAs, by weight[a]	Percent Anthracene (Sensitizer), by weight[a]	Cure Results
10	0	No cure
10	5	No cure

(a) Based on resin.

SECTION III

CONCLUSIONS

In this exploratory program, the UV-initiated cure of small test samples (2 inches by 2 inches by 3/4 inch) of a furan resin concrete was demonstrated. However, because of the high cost of the UV initiator (diphenyliodonium hexafluoroarsenate), the amount of initiator required to obtain complete cure results in a very expensive polymer concrete. Three approaches -- reducing the amount of initiator, use of catalyst, and use of alternate, more reactive initiators -- for reducing the cost of the UV-initiated furan concrete were investigated. None of these approaches, all of which would effectively reduce cost through reducing the amount of required initiator, yielded a completely cured furan concrete upon UV exposure.

Therefore, although the concept of obtaining a highly controllable furan concrete through UV-initiated cure appears to be feasible (proven only for small samples), the cost of the UV-curable system is too high to effectively compete with the other polymer concrete systems being considered in the Rapid Runway Repair Program.

SECTION IV

RECOMMENDATIONS

Based on (1) the demonstrated feasibility of UV-initiated cure of furan concrete, (2) the large degree of controllability gained from UV-initiated cure, and (3) the attractiveness of furan concrete with respect to low cost, high strength, and independence from fossil fuel supplies, it may be advantageous to carry out further efforts directed toward overcoming the problem of high cost.

In order to significantly reduce the amount of UV initiator (onium salt) required for complete cure and,thereby,reduce cost, the most important factor is the optimum production of the cure-initiating species (H^+). The following approaches are recommended as offering the best chances for obtaining this optimum production.

a. Increase the intensity of the 313 mμ and 366 mμ light reaching the surface of the polymer concrete through the use of a higher power lamp and/or through the focusing of the UV light using a reflector.

b. Use of metal flake to reflect the UV light and thereby increase its path length through the polymer concrete. An increase in path length results in a higher probability for absorption. Initiator species are not produced unless the onium salt and/or sensitizer absorb the UV light.

c. Use of iodonium or sulfonium antimonate salts whose hydrolytic stability is acceptable. Recall that the antimonate-containing salts produce a much stronger acid (initiator) than the arsenate-containing salts.

d. Use of catalysts (such as organic copper salts) for the sensitizer/onium salt initiation process.

e. Use of sensitizers other than thioxanthane. Certain organic dyes have been shown to be effective(Reference 10). Since most of these dyes have strong absorptions at wavelengths greater than 400 mμ, a visble light source could be used (visible region, approximately 400 to 700 mμ).

If one or a combination of the above approaches is successful, then the amount of required initiator can be further reduced through increasing the reactivity of the furan resin (addition of promoters and/or use of a furan system more reactive than Airkure® 06-00, if available).

A research program involving the recommended approaches and a modest level of effort should answer the question of overall feasibility of UV-curable furan concrete.

SECTION V

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APPENDIX A

DEFINITION OF BEER'S LAW

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DEFINITION OF BEER'S LAW

Beer's Law describes the fraction of an incident light beam at a particular wavelength which is absorbed upon passing through a solution containing an absorbing compound. The fraction absorbed depends on the concentration of the absorbing species (moles/liter) and upon the length of the path (cm) traversed by the light beam.

If I_0 represents the intensity of a light beam incident on a section of solution containing c moles/liter of an absorbing species, and if I represents the reduced intensity (transmitted intensity) of the beam after passing through b centimeters of the solution, then Beer's Law may be represented as:

$$\log I_0/I = \epsilon bc = A$$

In the above equation, ε is a constant (called the molar absorptivity) for the absorbing compound which represents the tendency of the absorbing compound to absorb a particular wavelength of radiation. A large ε value represents strong absorption. The logarithm of the ratio of the incident intensity to the transmitted intensity is called the absorbance of the solution, A. The absorbance increases directly with the path length traveled by the light beam and with the concentration of the absorbing compound.

1. CONCENTRATION OF THIOXANTHONE REQUIRED TO ABSORB ALL OF THE INCIDENT 313 nm AND 366 nm UV LIGHT

If a particular absorbing compound absorbs 99 percent of the incident light of a particular wavelength ($I_0 = 100$ and $I = 1$), then the absorbance value is 2 ($\log I_0/I = \log 100/1 = 2$). Therefore, for a given path length traversed by the light, the concentration (c) of thioxanthone needed to absorb 99 percent of the 313 nm and 366 nm incident light can be calculated (using Beer's Law) in the following manner.

<u>Known Values</u>

a. Path length = 2 cm (thickness of polymer concrete sample exposed to UV light)

b. For thioxanthone, $\epsilon_{313} = 1600$ and $\epsilon_{366} = 3000$

c. $A = 2$ (99 percent light absorption).

Calculation

For 313 mμ light:

$$A = \epsilon bc$$

$$2 = (1600)(2)(c)$$

$$1/1600 = c$$

$$6 \times 10^{-4} \text{ moles/liter} = c$$

For 366 mμ light:

$$A = \epsilon bc$$

$$2 = (3000)(2)(c)$$

$$1/3000 = c$$

$$3 \times 10^{-4} \text{ moles/liter} = c$$

- -

The concentration of thioxanthone used was 2.1×10^{-3} moles/liter which (based on the above calculations) is greater than that needed to absorb 99 percent of the incident 313 mμ and 366 mμ light with a path length of 2 cm. The presence of an excess of thioxanthone is an advantage because the aggregate present in the polymer concrete test samples may reduce the path length of the UV light through the sample. Therefore, to maintain an absorbance of 2, a reduction in path length would require an increase in the thioxanthone concentration ($A = \epsilon bc$).

2. COMPETITION BETWEEN ABSORBING SPECIES FOR INCIDENT UV LIGHT

If two compounds which absorb in the same UV wavelength region are present in a solution, the portion of the incident UV light of a given wavelength absorbed by each compound is calculated in the following manner.

a. Absorbances of compounds 1 and 2 at Xmμ are given by, $A_1 = \epsilon_1 bc_1$ and $A_2 = \epsilon_2 bc_2$. No other compounds are present which absorb at Xmμ

b. Portion of Xmμ light absorbed by compound 1 is $\epsilon_1 c_1/\epsilon_1 c_1+\epsilon_2 c_2$.

c. Portion of Xmμ light absorbed by compound 2 is $\epsilon_2 c_2/\epsilon_1 c_1+\epsilon_2 c_2$.

Therefore, if the concentration of compound 1 is much less than the concentration of compound 2 (which is the case for DPIHAs mixed with a candidate resin), compound 1 will be able to effectively compete with compound 2 for the λ_m light only if the tendency (ε) of compound 1 to absorb λMμ light is significantly greater. That is, at equal concentrations, the absorbance of compound 1 must be considerably greater than the absorbance of compound 2 at λ_m.

The following calculation of the portion of incident 250 mμ absorbed by 10-percent by weight DPIHAs (based on resin) mixed with Airkure® 06-00 will illustrate the effects of ε and c on competitive absorption.

Known Values

a. For DPIHAs at 250 Mμ, $a_1^* = 50 \times 10^3$ (from UV spectrum).

b. For Airkure® 06-00 at 250 mμ, a_2 7×10^3 (from UV spectrum).

c. Mixture consists of 10 g DPIHAs and 100 g Airkure® 06-00.

d. Density of Airkure® 06-00 is approximately 1 g/ml.

e. Path length, b, is the same for the two species.

Calculations

Portion of 250 mμ light absorbed by DPIHAs = Y

$$Y = \left(\frac{a_1c_1}{a_1c_1 + a_2c_2}\right) = \frac{(50 \times 10^3)(10\ \text{g}/100\ \text{ml})}{(50 \times 10^3)(10\ \text{g}/100\ \text{ml}) + (4 \times 10^3)(100\ \text{g}/100\ \text{ml})}$$

$$Y = \frac{50 \times 10^3}{90 \times 10^3} = .55$$

Therefore, since a_1, is significantly greater than a_2, 10-percent by weight DPIHAs in Airkure® 06-00 will absorb approximately 55 percent of the incident 250 mμ light.

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* Since the exact chemical nature of Airkure® 06-00 is not known, the concentration term in Beer's Law was expressed in g/1000 ml rather than moles/liter. When concentration is expressed as g/1000 ml, the term a (absorptivity) is substituted for ε (molar absorptivity).

APPENDIX B

UV SPECTRA OF CANDIDATE RESINS, DPIHAs AND THIOXANTHONE

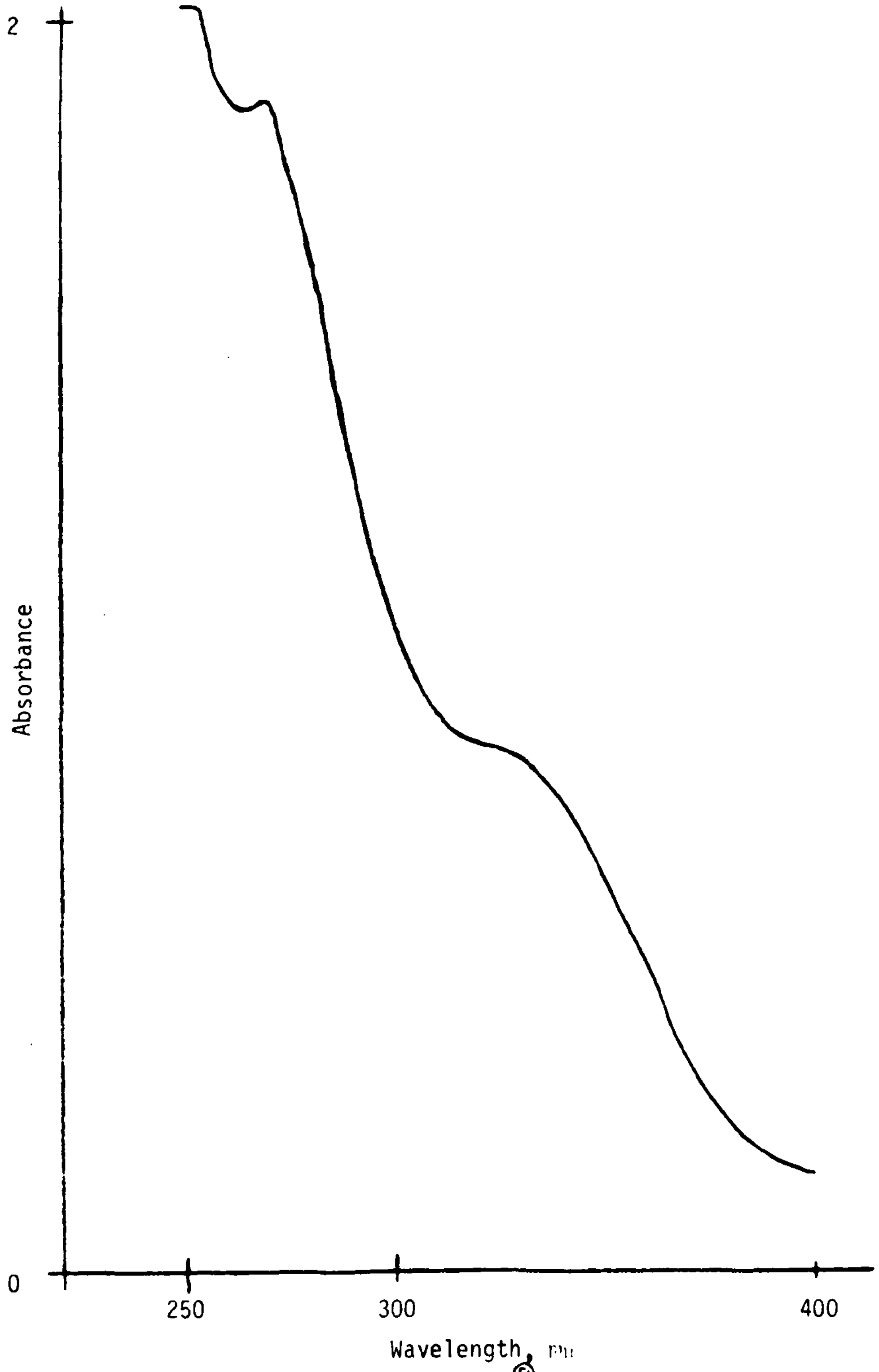

Figure B-1. Chem Rez® 200 UV Spectrum

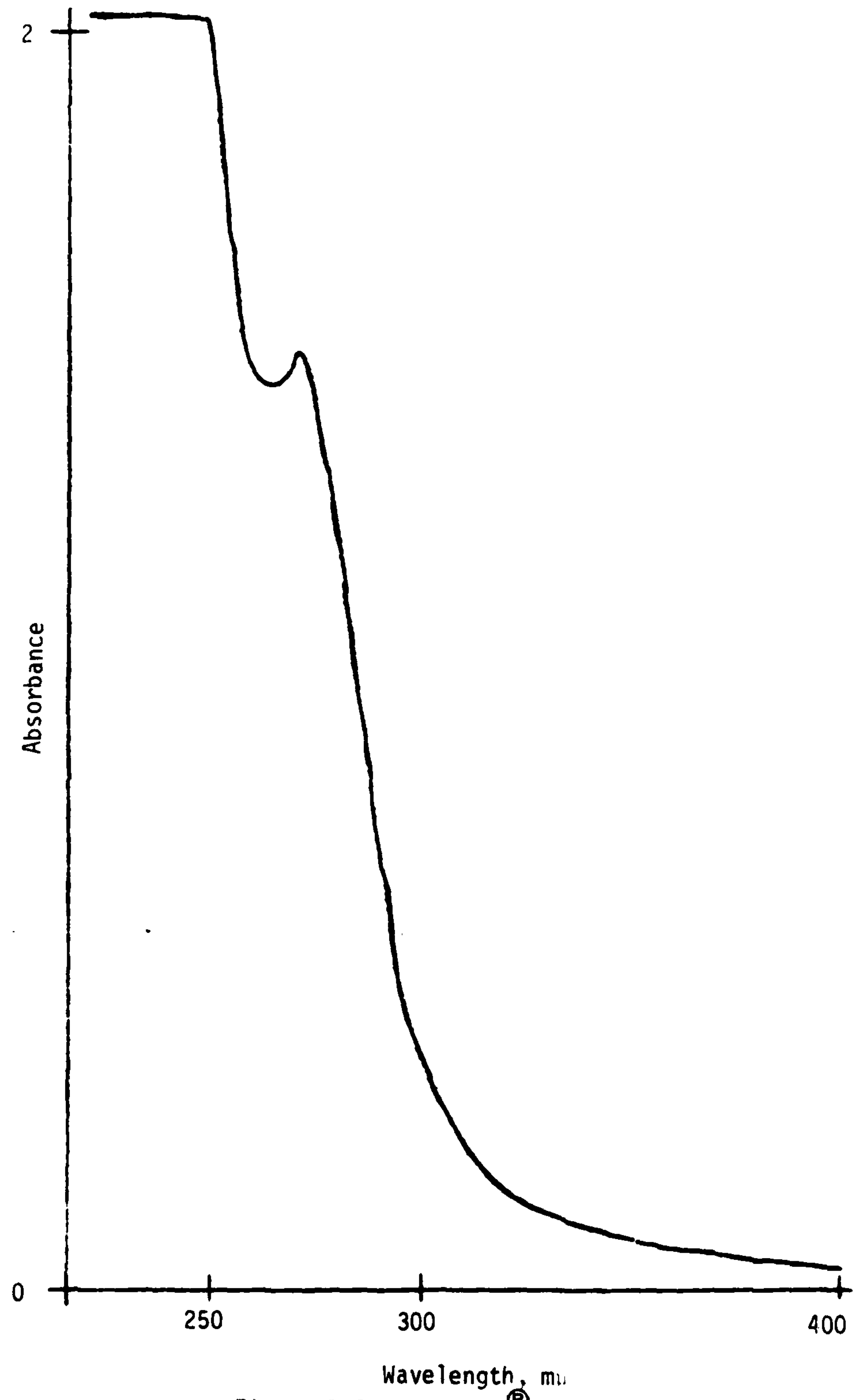

Figure B-2. Chem Rez® 201 UV Spectrum

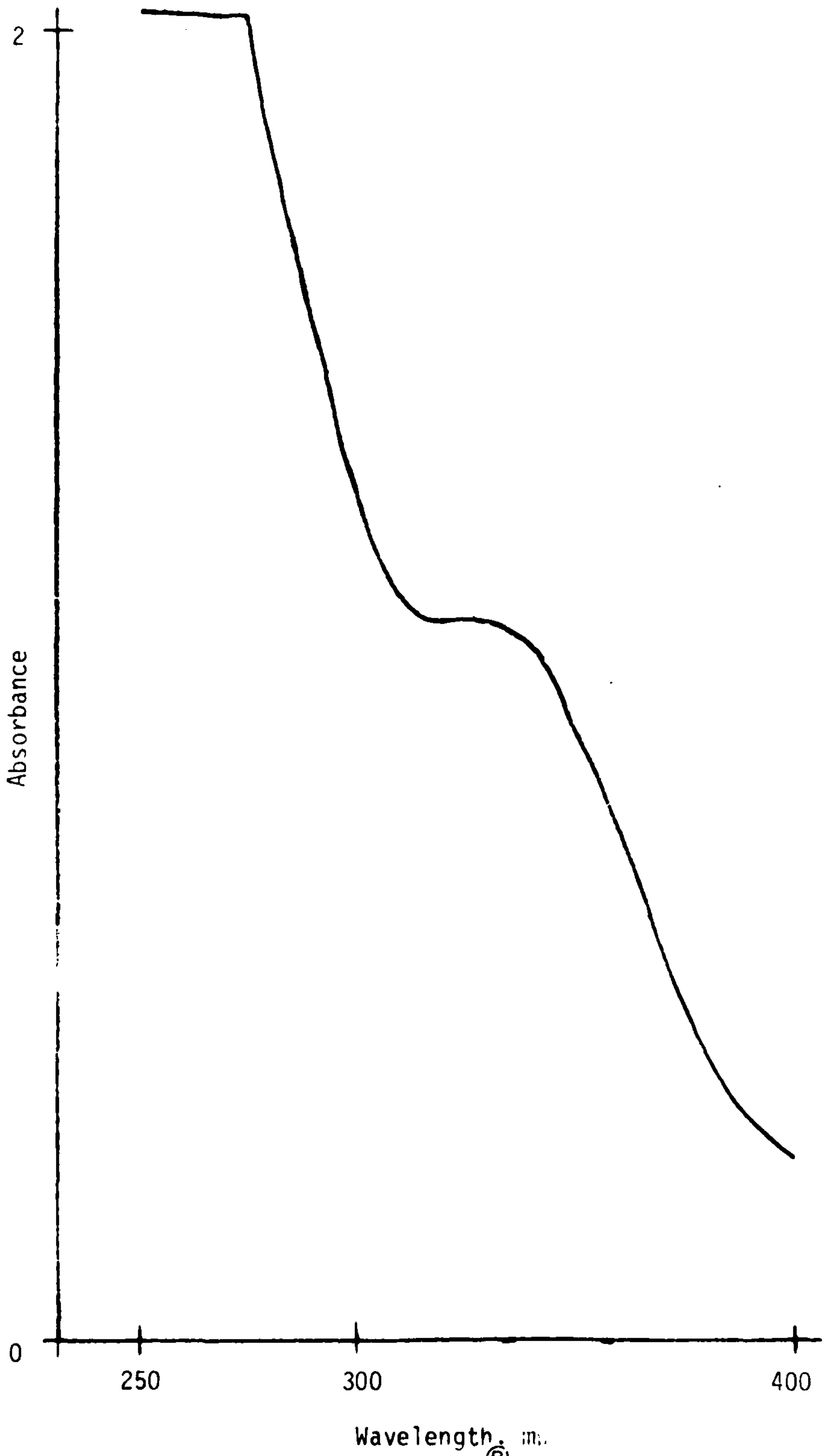

Figure B-3. Chem Rez® 230 UV Spectrum

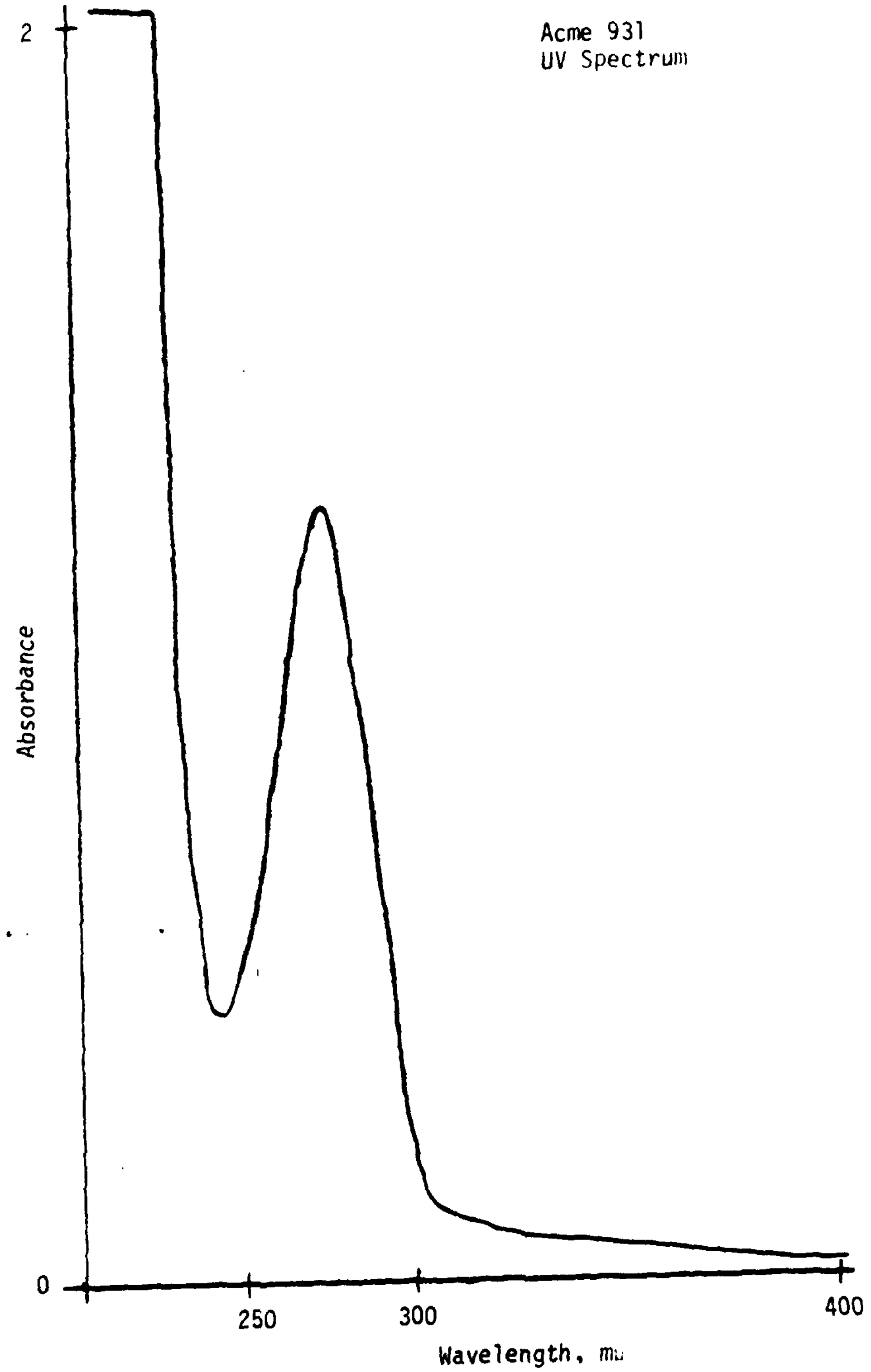

Figure B-4. Acme® 931 UV Spectrum

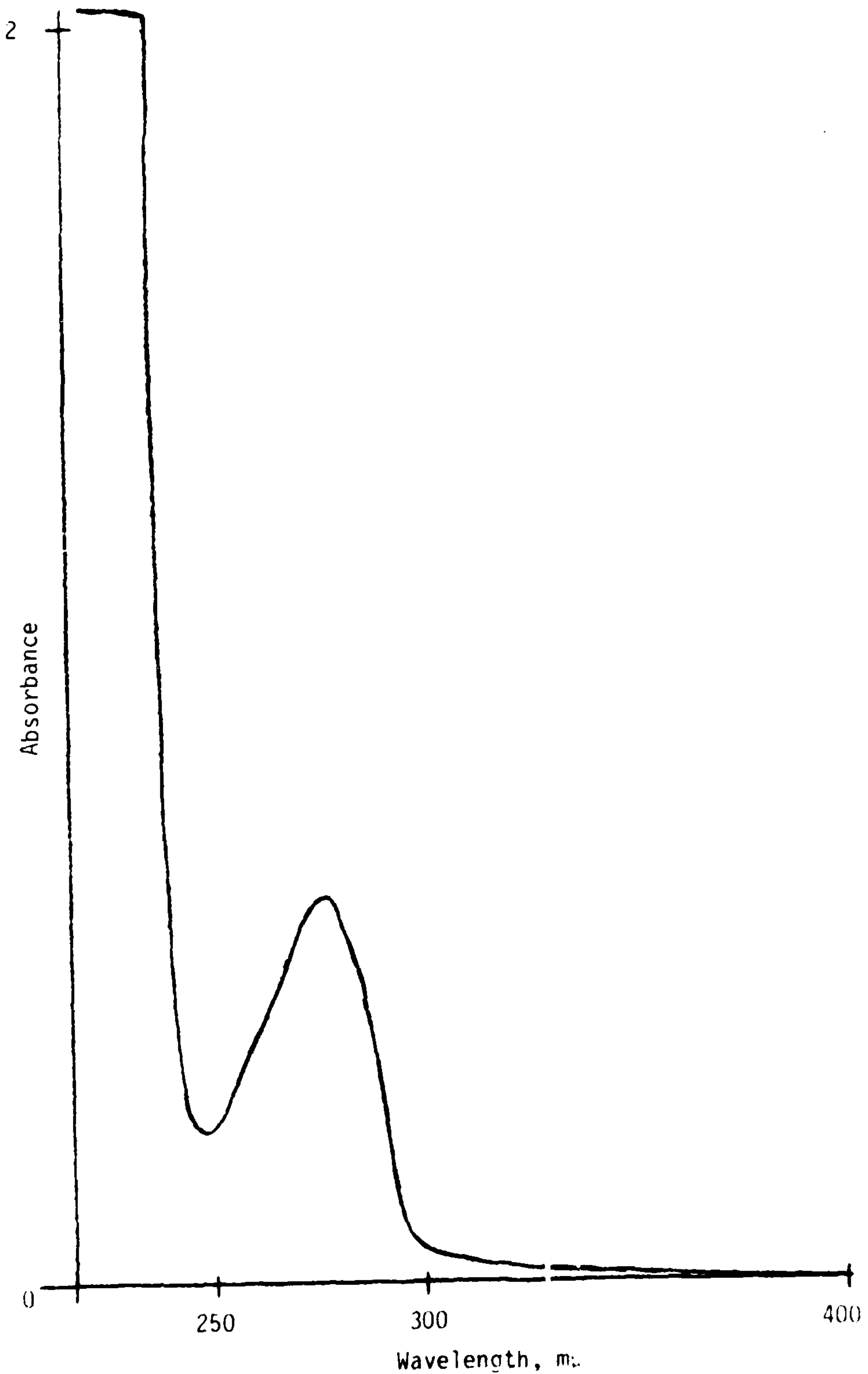

Figure B-5. Airkure® 06-00 UV Spectrum

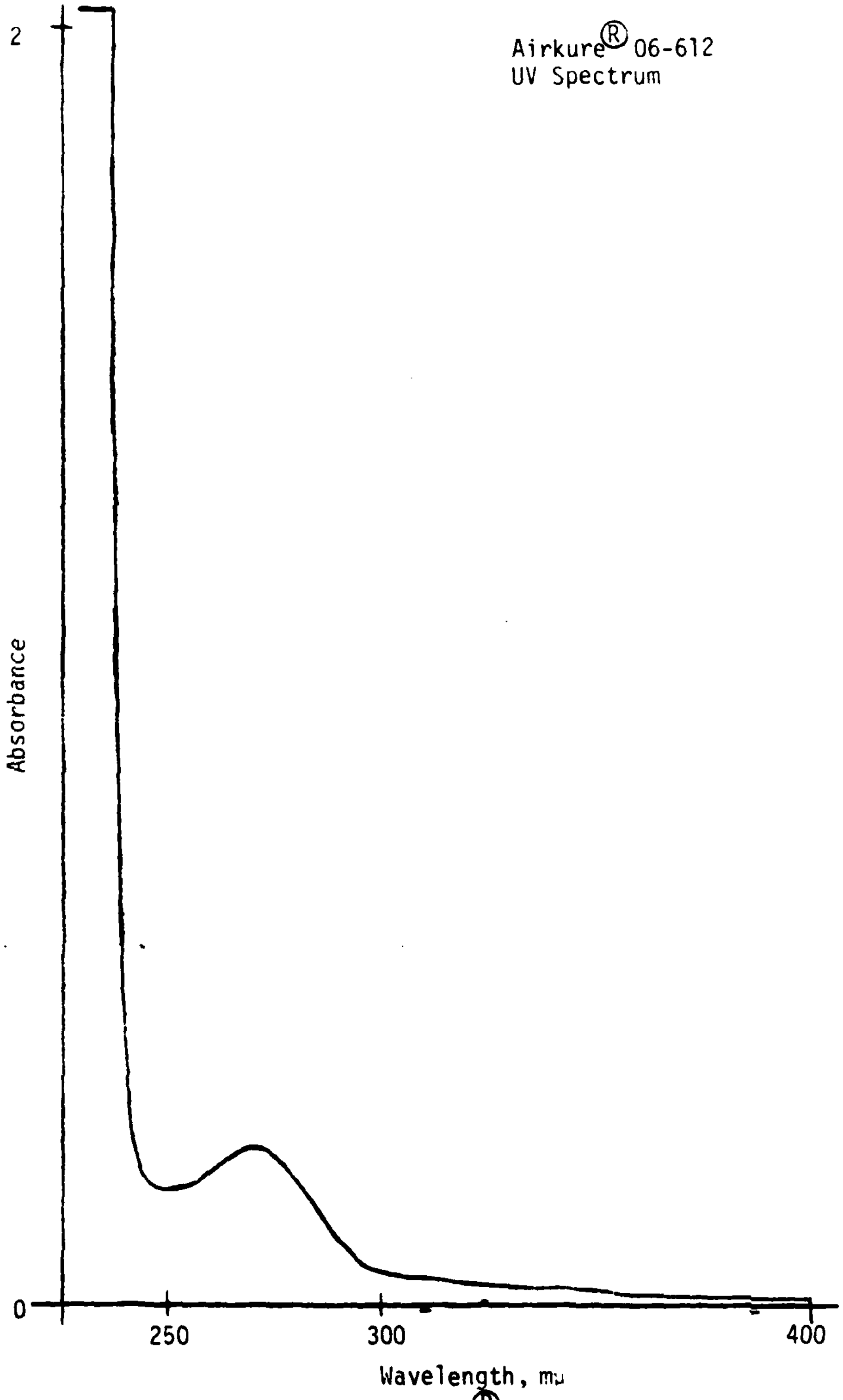

Figure B-6. Airkure® 06-612 UV Spectrum

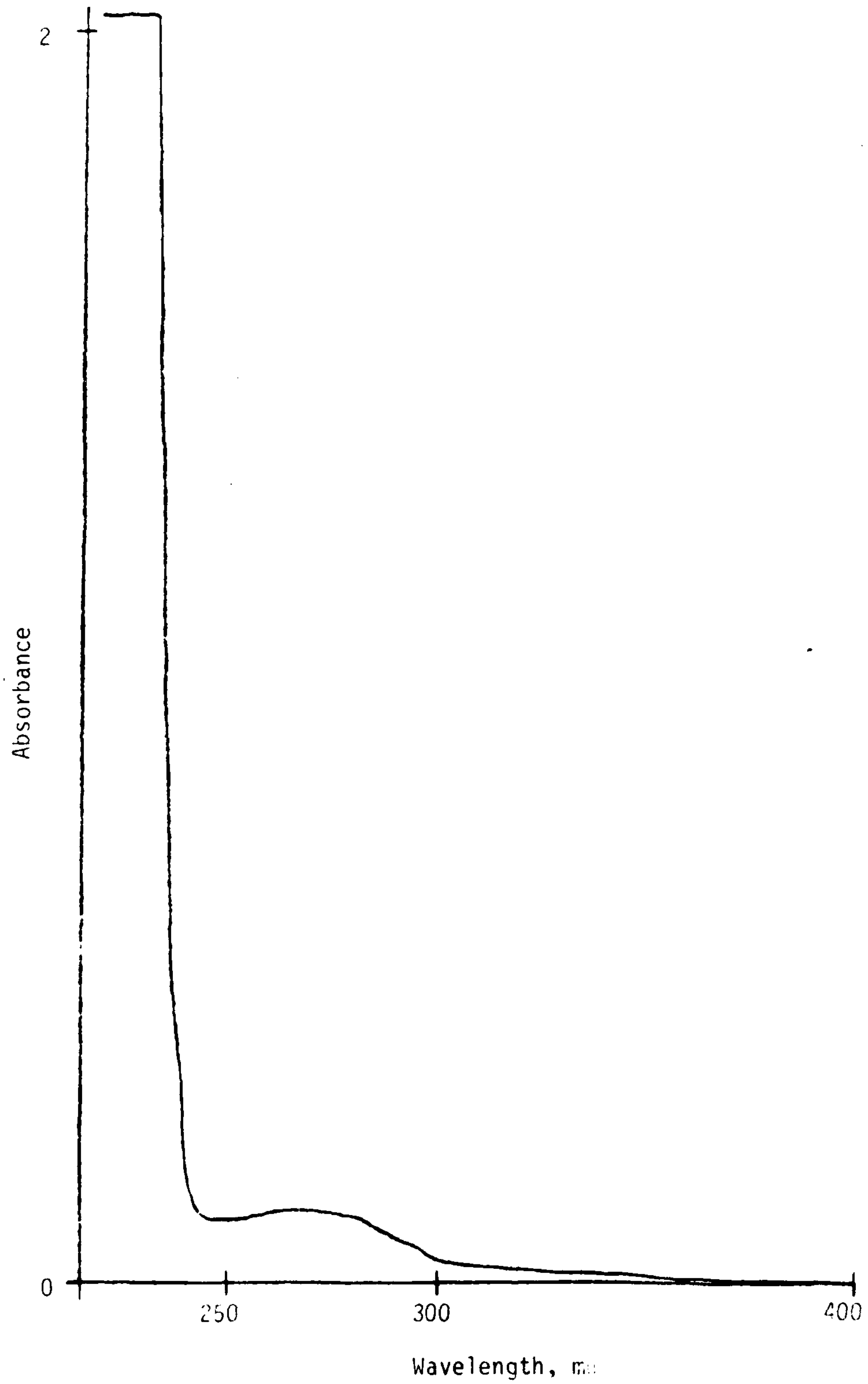

Figure B-7. Furfuryl Alcohol UV Spectrum

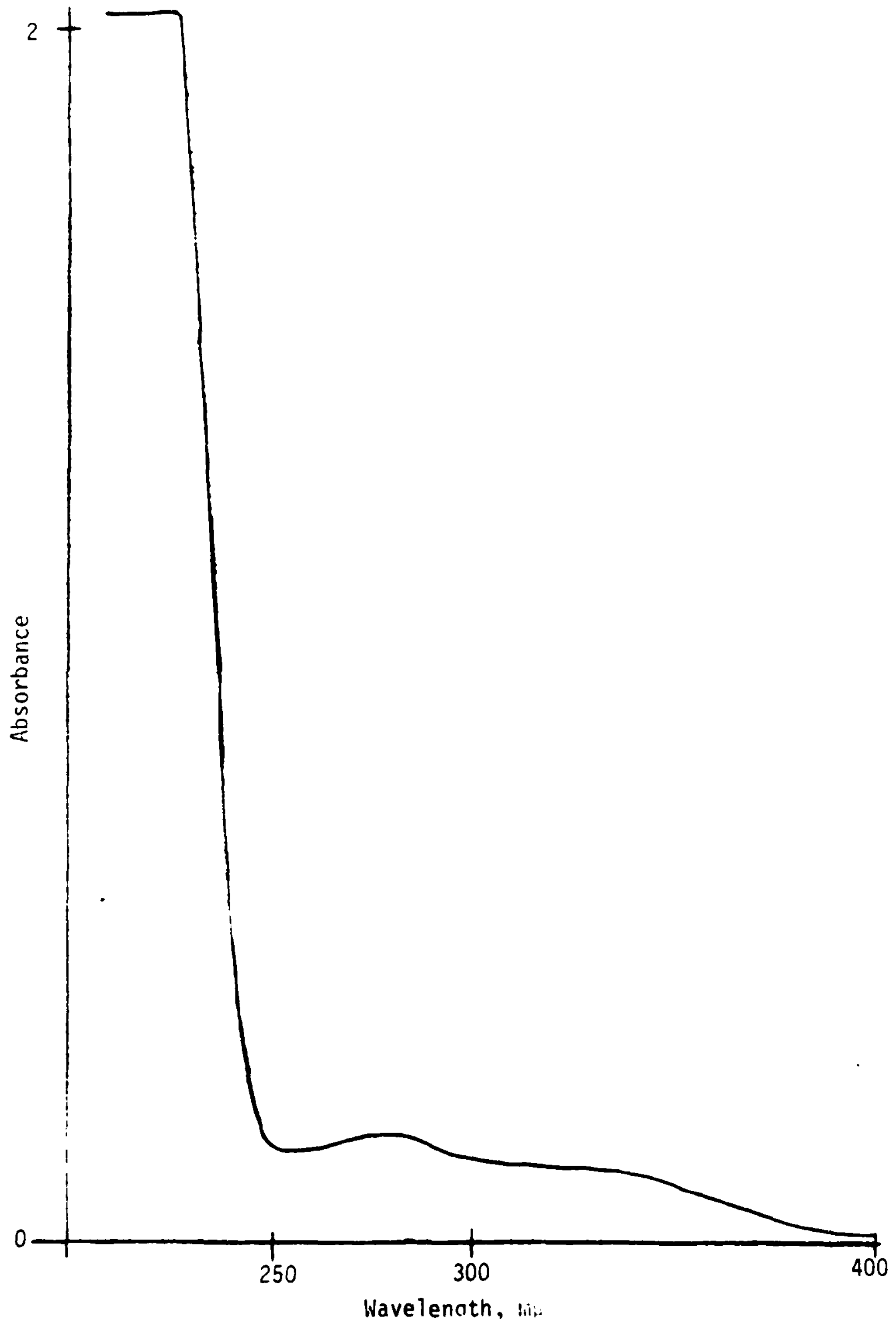

Figure B-8. Corelube® CL1-1000 UV Spectrum

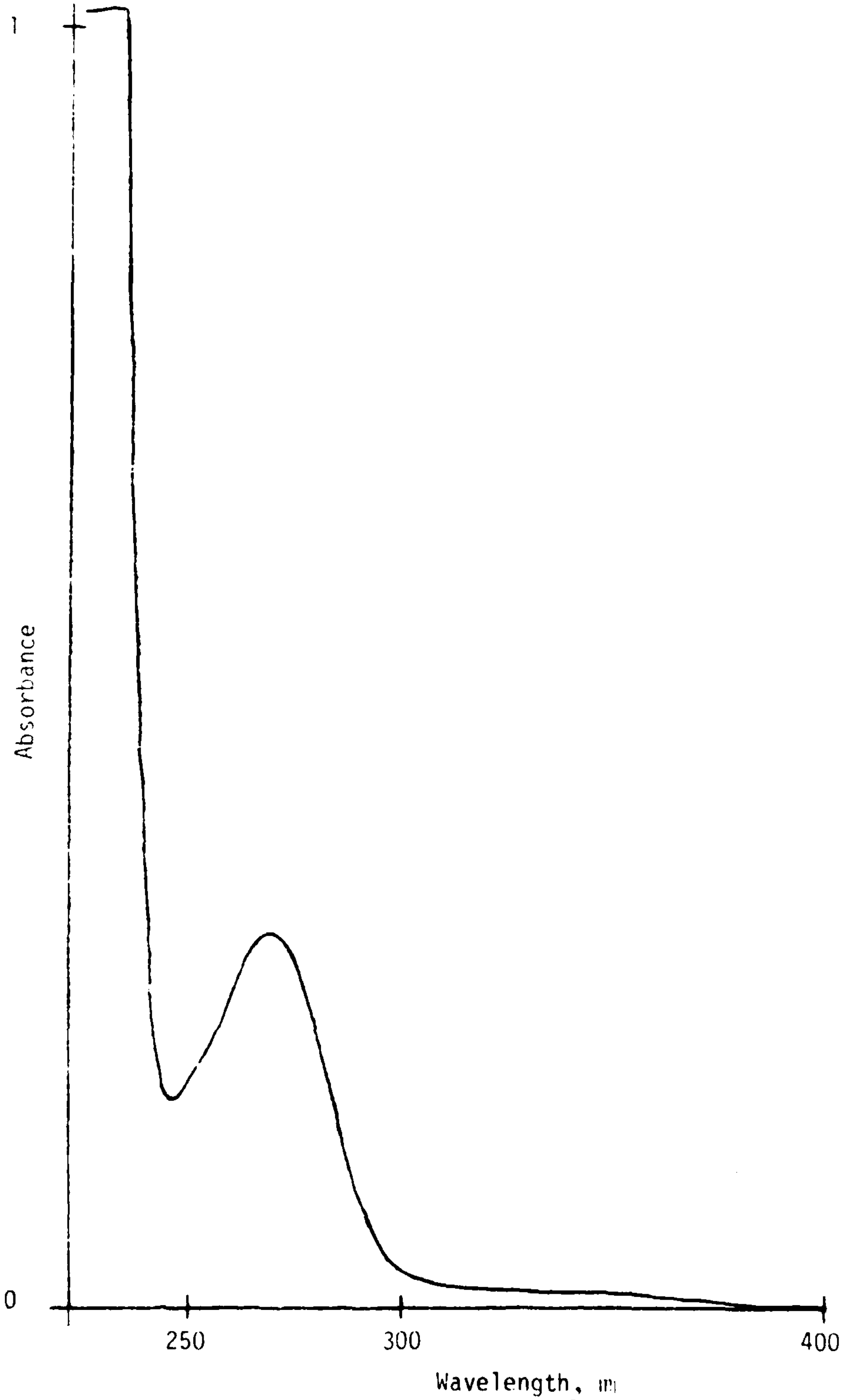

Figure B-9. Airkure® 06-22 UV Spectrum

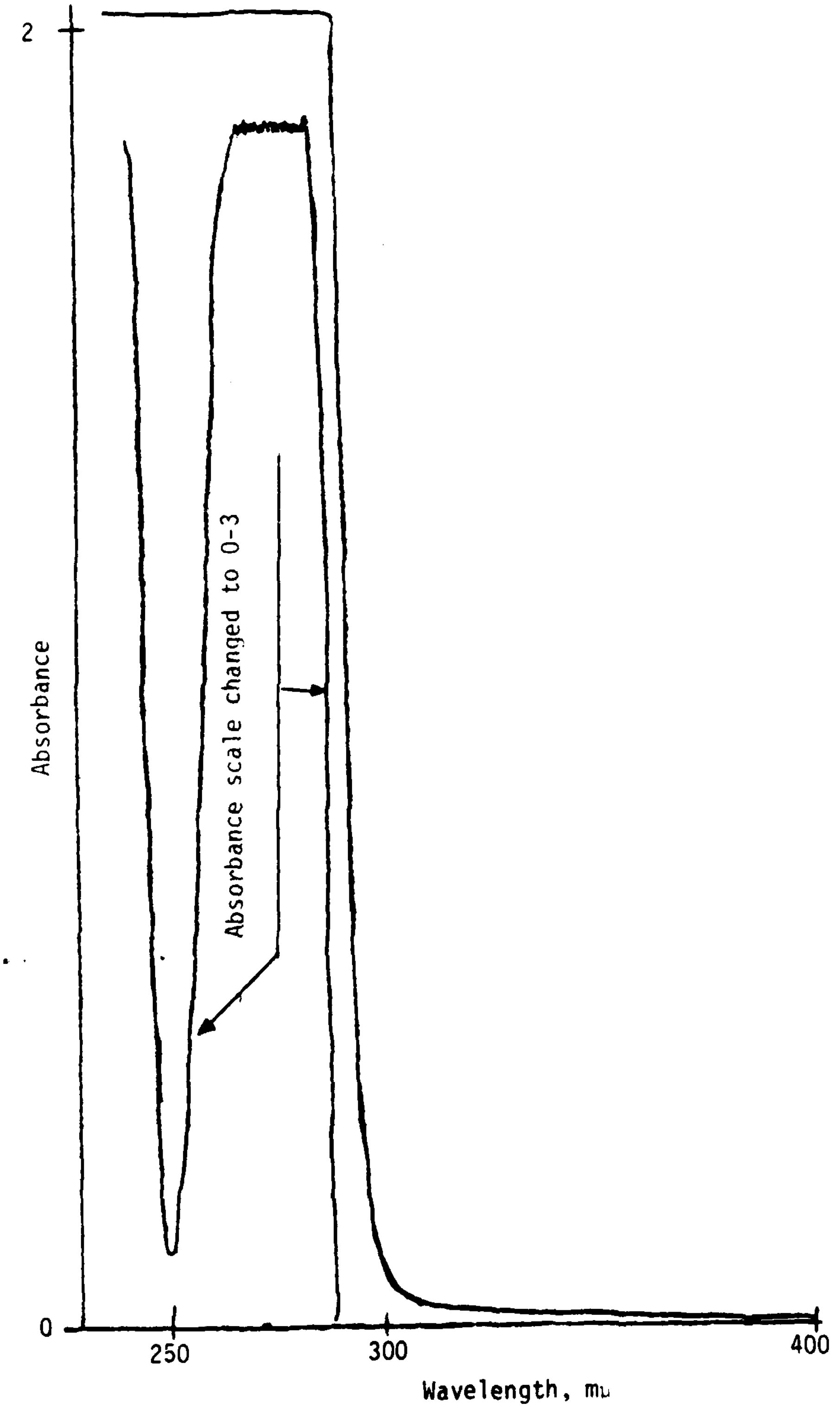

Figure B-10. Epon® 828 + Heloxy® 69 UV Spectrum

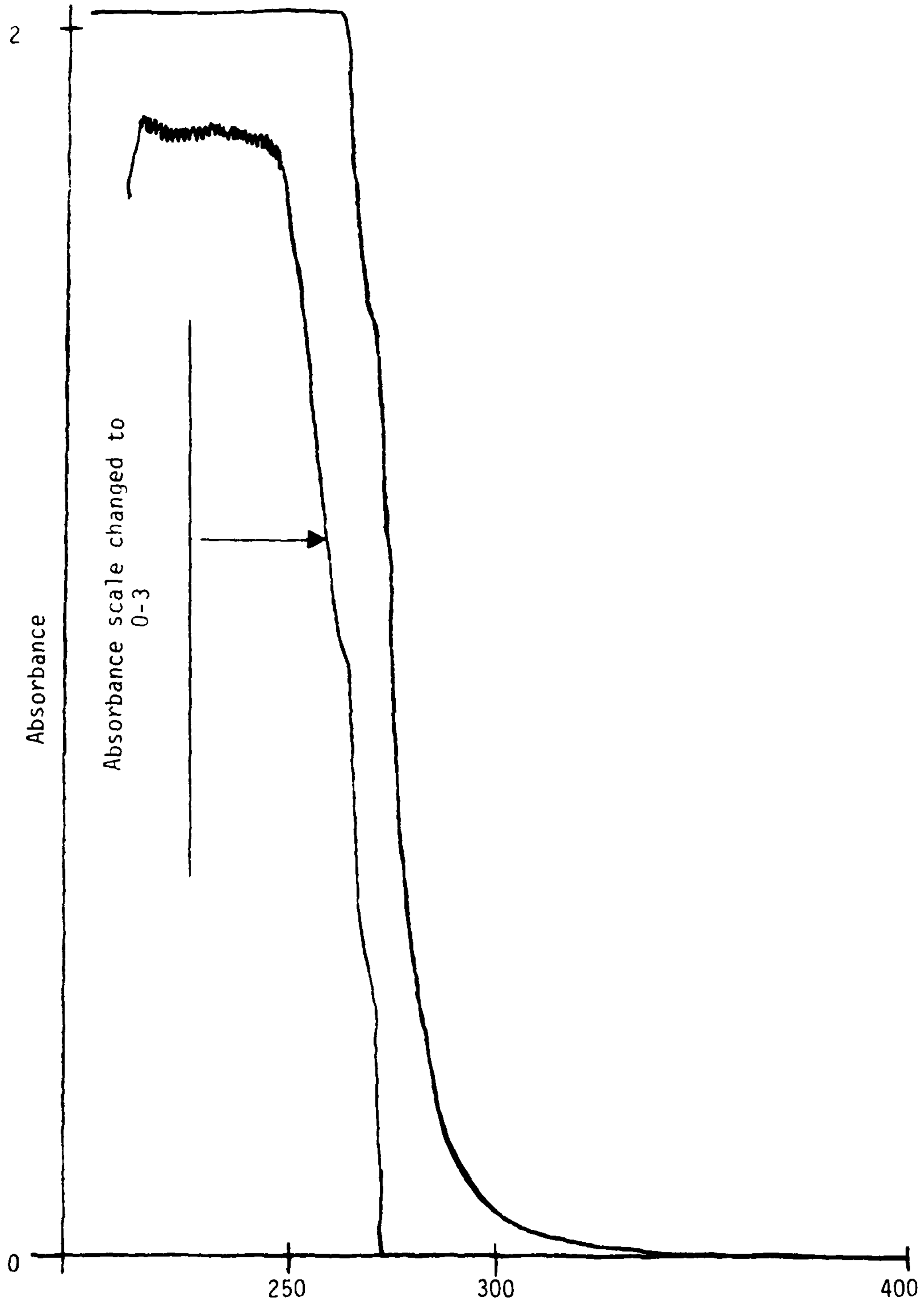

Figure B-11. DPIHAs UV Spectrum

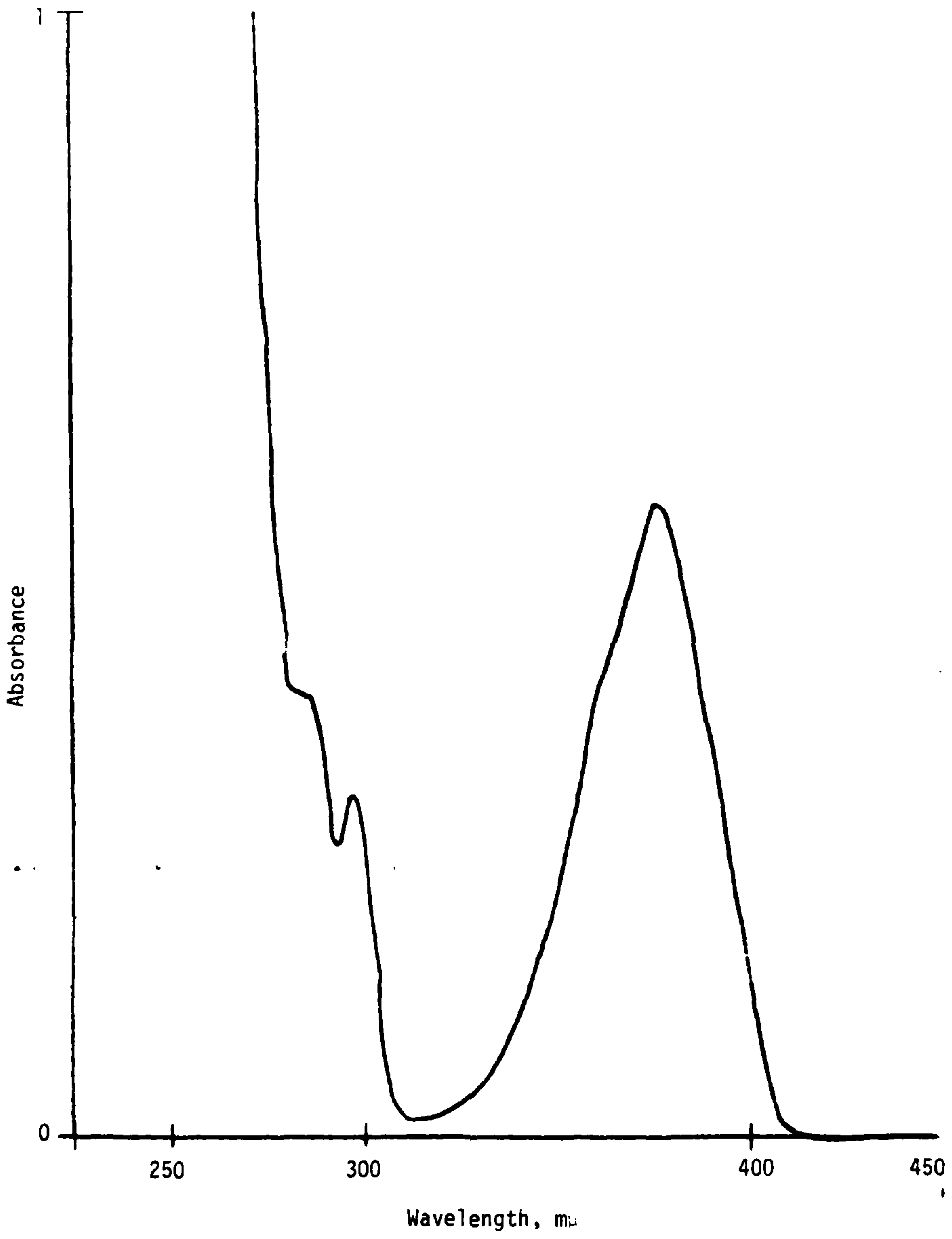

Figure B-12. Thioxanthone UV Spectrum

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