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NEW METHODS FOR THE STUDY OF FILM DEGRADATION AND THEIR APPLICATION TO THE STUDY OF PHOTOOXIDATION OF ALKYD FILMS

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Film deterioration is a broad field. Organic coatings are affected by, among other things, heat, water, chemicals, mechanical abrasion, and ultraviolet light. The relative importance of each of these agents in the overall deterioration of protective coating will depend upon the use for which the coating is intended.

Organic films used as exterior finishes are, naturally, most susceptible to the action of ultraviolet radiation, and it is this aspect of film deterioration that I should like to discuss this evening.

There are two main benefits to be gained from a study of photodegradation of a film-forming polymer. First, from a knowledge of its rate of degradation, we may assess its potential suitability for exterior coatings. Second, from a knowledge of the mechanism of the chemical processes, we may learn weak points in the polymer structure, and thus direct our efforts to synthesize more durable polymers.

There has been a great deal of work done on the oxidation of drying oil-type materials by laboratories concerned with the study of edible fats, by the laboratory of the British Rubber Producers, by the Naval Research Laboratory, and by various paint producers, both in this country and abroad. While the final definition of the process may be yet to come, we might consider the work of Farmer which postulates the initial formation of an

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α-methylenic hydroperoxide which can then undergo various secondary reactions to form ethers, aldehydes, carboxylic acids, peroxides. In any event, a consistent explanation must take into account the absorption of oxygen in the drying film, the decrease in unsaturation and the shift of the 1,4-diolefin to a conjugated structure. It is our feeling that the degradation process in a drying oil is merely a continuation of the drying reaction sequence. The absorption of ultraviolet light activates the molecule and facilitates the reaction with oxygen. The oxygenated product is subject to chain scission and this, in turn, leads to the elimination of small molecules, water, CO, CO_2, formic acid and other low molecular weight organic fragments.

The photooxidation of nitrocellulose and other cellulose derivatives has also been investigated, most recently by Saur at General Motors. They have observed a denitration of nitrocellulose to cellulose, accompanied by oxidation to celluronic acid and chain scission to cellobiose and cellotriose. Volatile decomposition products included water, CO_2 and CO as oxidation products of the original lacquer and oxides of nitrogen which are reduction products of the nitrate in the lacquer.

The work of our laboratory in the field of photo-oxidative degradation has been largely concentrated on the drying-oil alkyds, and it is our own studies which I should like to discuss in some detail. However, before discussing results, perhaps a short description of our experimental methods is in order. The classical techniques for studying

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polymer degradation, particularly those involving molecular weight changes, are not suitable for a crosslinked film. Accurate weight loss measurements are extremely difficult on supported films because of the weight of the substrate, and free films become so brittle on exposure that they are difficult to manipulate. On the other hand, the conventional methods for observing degradation in paint films are essentially empirical and qualitative, frequently lacking the accuracy and precision required for a kinetic study. Yet these manifestations of degradation, notably gloss loss, are the factors which largely determine the suitability of a particular coating for exterior uses. This loss of gloss has been shown to occur as the top layer of clear polymer is eroded away, leaving pigment particles on the surface. It occurred to us then that there might be a simple relationship between the gloss loss of a pigmented film and the erosion rate of a very thin layer of clear vehicle. If the thickness of the "thin layer" was of the order of the wavelength of light, these films should show interference phenomena and the thickness changes which accompany irradiation by ultraviolet light might, therefore, be observed interferometrically with high precision. This proved to be a simple, non-destructive, and accurate (to 0.1%) method of studying the rate of alkyd degradation. The use of infrared spectroscopy to follow the chemical changes occurring in the film during irradiation has become a standard procedure.

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It might be worthwhile to describe our experimental procedure for preparing and characterizing these thin films. The first slide shows the sample preparation. Chrome plated microscope slides were suspended in a tube containing polymer dissolved in a volatile solvent, and the solution was drained slowly. The thickness of the film deposited on the mirror depends on the concentration of the polymer solution and the rate of flow. With a little practice, an operator can control the thickness to within a few per cent of the desired value, with local variations of not more than 0.5% from place to place in the film. The principal experimental requirement is extreme cleanliness; dust particles cause marked local inhomogeneity in film thickness.

The next slide shows schematically the reflection of light from a thin film to produce interference colors. An incident beam strikes the film at (a) and is partially transmitted and partially reflected. The phase relation between the two parallel beams at (f) and (c) determines whether reinforcement or interference will occur, and the phase difference is a function of the thickness of the thin film, so that the thickness may be calculated from the formula

$$\frac{\Delta M}{2n} \quad \frac{\lambda_1 \lambda_2}{\lambda_2 - \lambda_1}$$

where ΔM is the number of reflection maxima (or minima) in the interval $\lambda_2 - \lambda_1$. The reflectance measurements may be made on any visible spectrophotometer which includes the

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spectral component. A typical reflectance spectrum is shown in the next slide. The maxima and minima can be estimated visually, but precision can be considerably improved if the peaks are located geometrically, as shown in the next slide. Sensitivity and accuracy are about constant in the range 3,000-10,000Å. The greater sharpness of the peaks for thicker samples is balanced by the lesser displacement of these peaks for the same thickness change.

Ultraviolet exposures were made in air under a Hanovia 125 watt medium pressure mercury arc on a small turntable with stages at two distances from the lamp. The ratio of the light intensity at the two levels was measured as 3/1. Wavelength was controlled with various Corning transmission filters, so that we can describe the light as >2000Å (unfiltered), >2500Å, >3000Å, and >3500Å. Ambient temperature was about 40°C. Two samples, one twice the original thickness of the other, were exposed side by side, so that, with a total of sixteen samples, the effect of wavelength, intensity, and film thickness could be determined.

The particular alkyd used in this work was a linseed-chinawood oil alkyd, 50% oil length, acid number 18, without the addition of any drier. The films were baked in air at 120°C for one hour before exposure. The results which were obtained are, of course, specific to this resin; but the experimental procedure is of general application, and should supply the same type of information about any polymer of interest.

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The rate of erosion of this alkyd at all wavelengths is approximately proportional to the incident light intensity, as found earlier. The next slide shows a tabulation of the ratio of exposure hours required to reach the same per cent film loss for samples of the same initial thickness at the two light intensities.

The effect of wavelength on the rate of erosion is shown on the next slide. The figures listed here are the Angstroms eroded from a 10,000Å film after 44 hours exposure to the various wavelength distributions of ultraviolet light whose total energies are also given. Total energies transmitted by the various filters were measured by a thermopile calibrated against a National Bureau of Standards light bulb. Shorter wavelengths are seen to be increasingly effective in producing thickness changes, but if energy absorbed in any wavelength interval is compared to the thickness change produced by the same interval, the efficiency is seen to be relatively constant, as shown in the last column.

The effect of wavelength on the kinetics of the degradation process is shown in the next slide. The reaction under unfiltered light is plotted at one-third the intensity of the others to use the same coordinates. These short wavelengths give a true surface reaction, independent of thickness and linear with time, since the light is so strongly absorbed in the surface layer that the interior layers, even of these thin films, are not irradiated by these wavelengths. Typical data for unfiltered light are given in the next slide, and the lack of dependence on thickness is unmistakable.

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Longer wavelengths give rates of film loss which are not simple mathematically. However, for films of different original thickness, the loss of thickness at a given time is proportional to the original thickness as shown in the next slide. This suggests a bulk reaction analogous to a kinetic first order. The next slide shows our attempt to calculate a first order rate constant for a film irradiated with wavelengths >2950Å. A similar decrease in rate with time of exposure was obtained for all samples irradiated with wavelengths above 2500Å. This is interpreted as indicating a bulk reaction, with the selective oxidation of the more reactive groups leaving a film of progressively increasing stability toward further oxidation.

From these rate measurements it was suggested, as outlined above, that the chemical nature of the films was changing during exposure. To characterize the degradation process more fully, we studied these chemical changes by infrared spectroscopy. The spectroscopic changes which occur in an alkyd film upon exposure to wavelengths >2500 are shown in the next slide. A detailed description of this spectrum has been given many times before; let us consider only the 2.8μ hydroxyl stretching, the 3.4μ aliphatic C-H stretching, the 5.8μ carbonyl stretching, and the 13.5μ o-disubstituted aromatic deformation vibrations. Qualitatively we observe a broadening of the hydroxyl and carbonyl, undoubtedly resulting from the formation of complex oxygenated products, and an increase in the general absorption from 8 to 10μ, also probably attributable to singly- and doubly-bonded oxygen. More informative, we

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feel, are the intensity changes which accompany the photo-oxidative process. These we have measured as peak intensities only. While this is a drastic approximation, especially for hydroxyl groups, this simple treatment yields the very interesting results shown in the next slide. The steady decrease of the aliphatic C-H groups with the concomitant increase in hydroxyl and carbonyl groups is interpreted as the oxidation of the drying oil carbon-hydrogen groups to hydroperoxides, alcohols, ketones and acids. These latter groups first increase, and then as the C-H groups become fewer, their rate of decomposition exceeds their rate of formation, in a manner characteristic of the intermediates in a chemical reaction. These complex carbonyls, especially if conjugated, as for example, vicinal dicarbonyls, decompose with chain scission to produce eventually volatile products, free radicals, and new olefins or ketones which are subject to repetition of the oxidation process.

The aromatic portion of the polymer seems more stable than the aliphatic portion at longer wavelengths; but under unfiltered light where it absorbs energy directly, it decomposes rapidly and even preferentially. If the per cent decrease in the 3.4μ band is plotted against the decrease in the 13.5μ band at the same exposure time for various wavelengths, as shown in the next slide, several conclusions are suggested. First, the reaction is fundamentally different at very short wavelengths; this was also observed in the thickness loss experiments. Second, the decreasing slope of both of these curves indicates that the aliphatic portion of the molecule is becoming progressively more stable

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to photodegradation. The stabilization of the polymer predicted earlier by the kinetic analysis of the film thickness data has now been localized within the molecule. Third, a comparison of these two curves suggests that, at short wavelengths, the phthalate is decomposed directly, while at longer wavelengths at which the phthalate is transparent, its decomposition is a secondary process sensitized by the decomposition some portion of the aliphatic groups. The absence of a band at 3.2 μ which is present in an unbaked alkyd indicates that the residual unsaturation in a crosslinked film is very low, and, therefore, it is probable that the site of attack is the tertiary hydrogen which occurs on each chain at a crosslink. Certainly either residual unsaturation or more probably secondary structures arising from the double bonds constitute the reactive sites. A simultaneous study of the degradation of a film of the comparable stearic acid alkyd showed that it was much more durable toward radiation in the sunlight region not only in the aliphatic portion, which was different, but also in the aromatic portion which was identical to the drying oil alkyd. This is, we feel, strong evidence for the photosensitization mechanism of phthalate decomposition in drying oil alkyd films.

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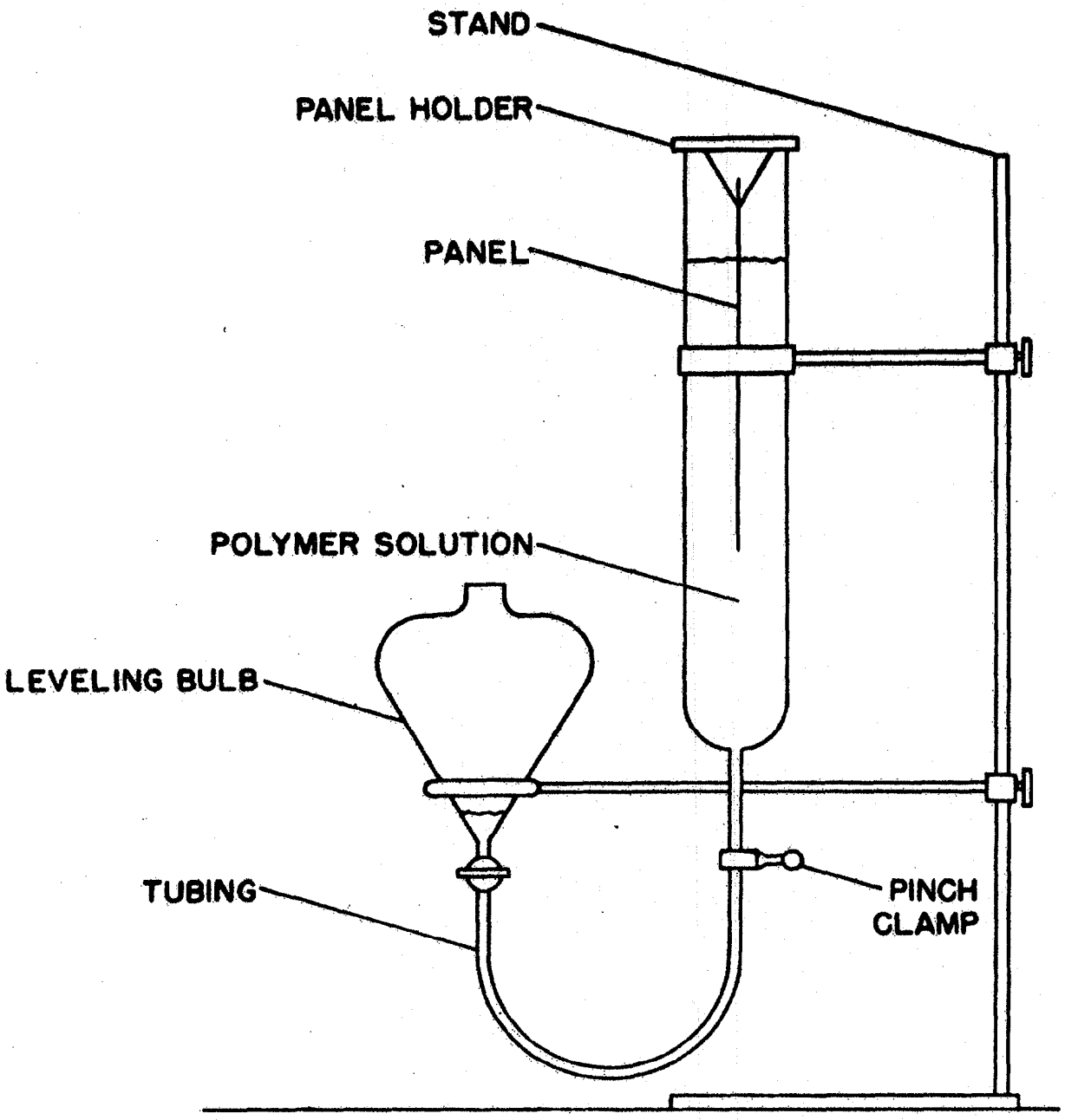

FIGURE I

DIPPING APPARATUS

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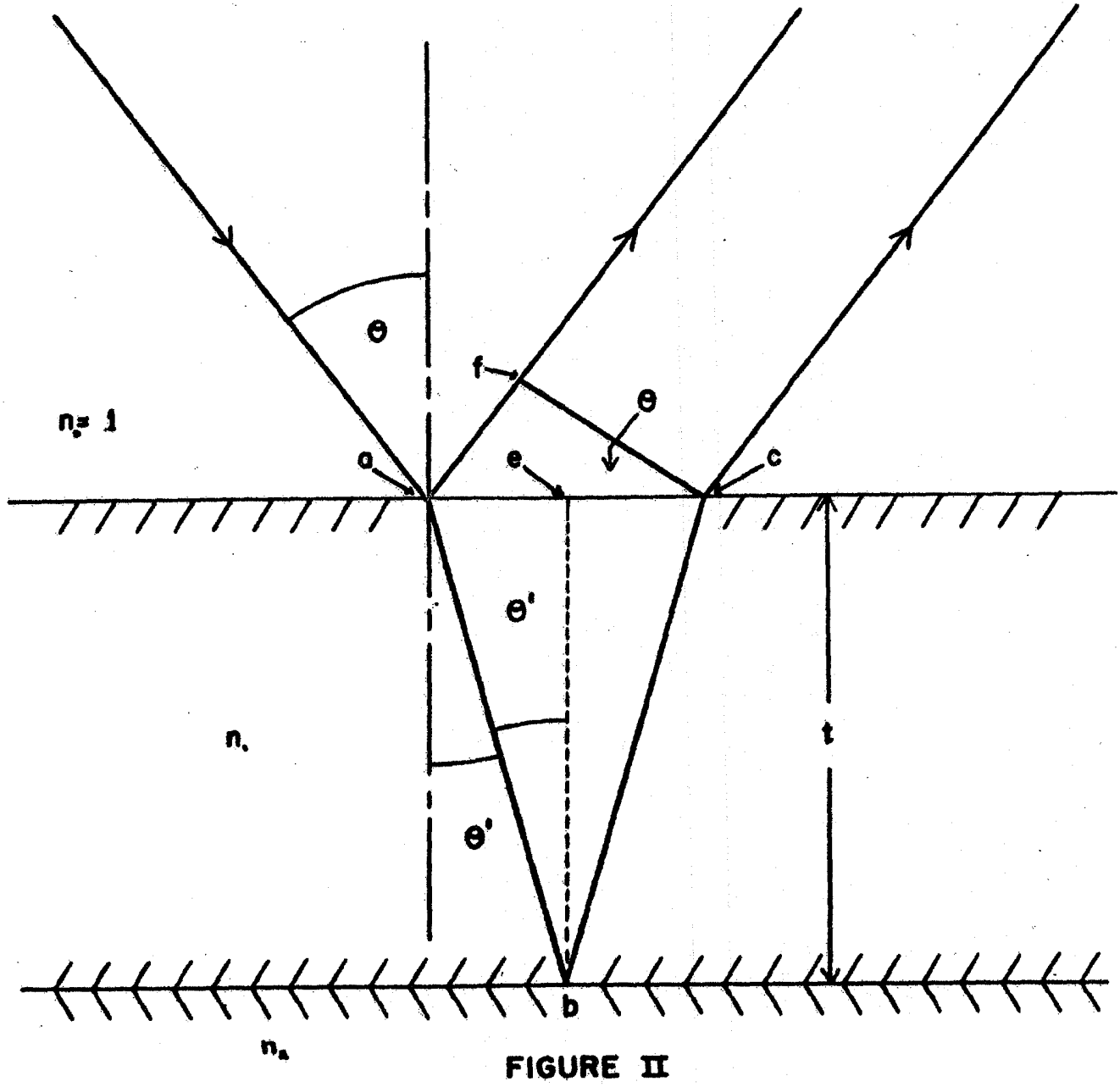

FIGURE II

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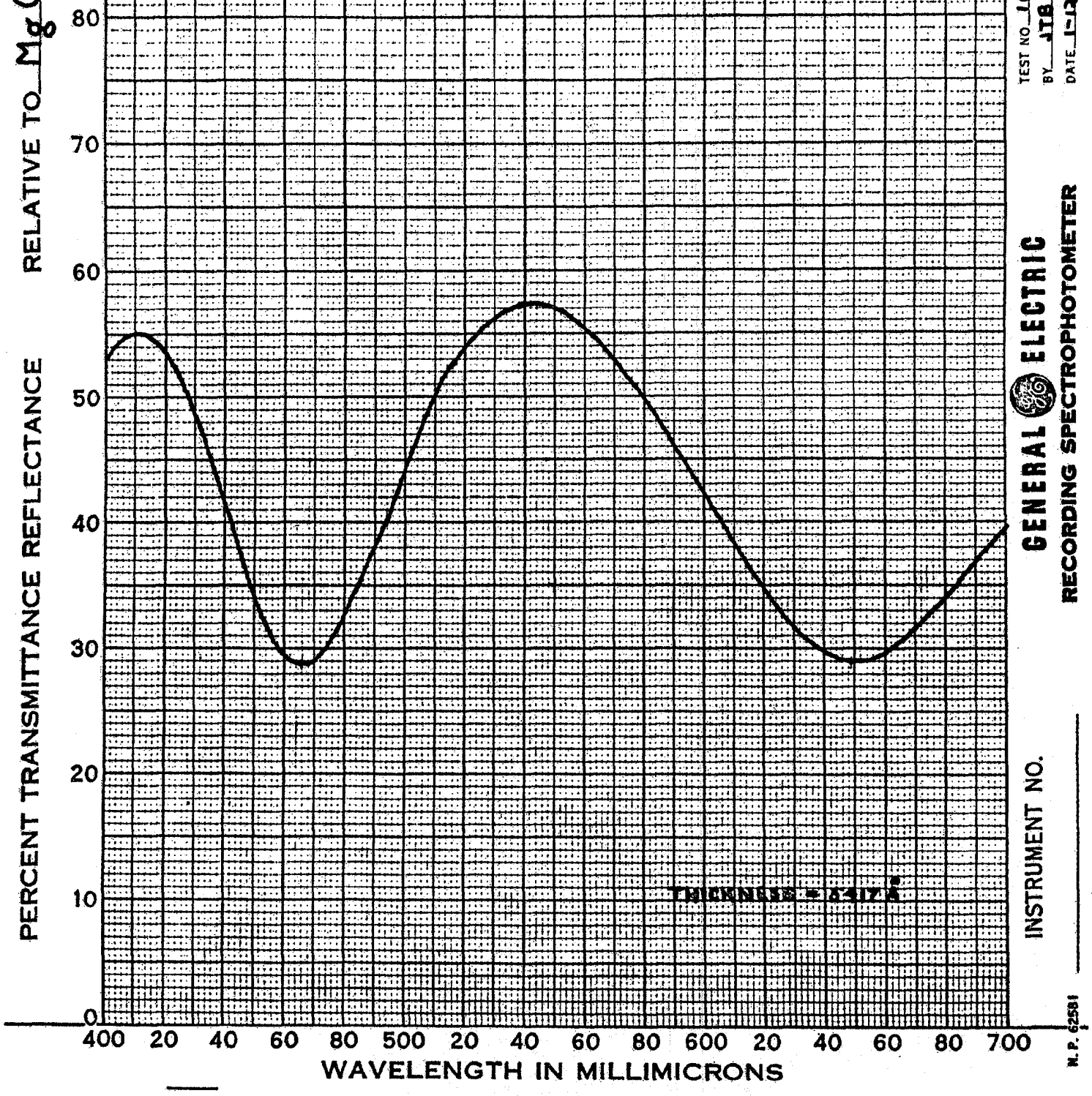

FIGURE III- REFLECTANCE SPECTRUM OF THIN FILM

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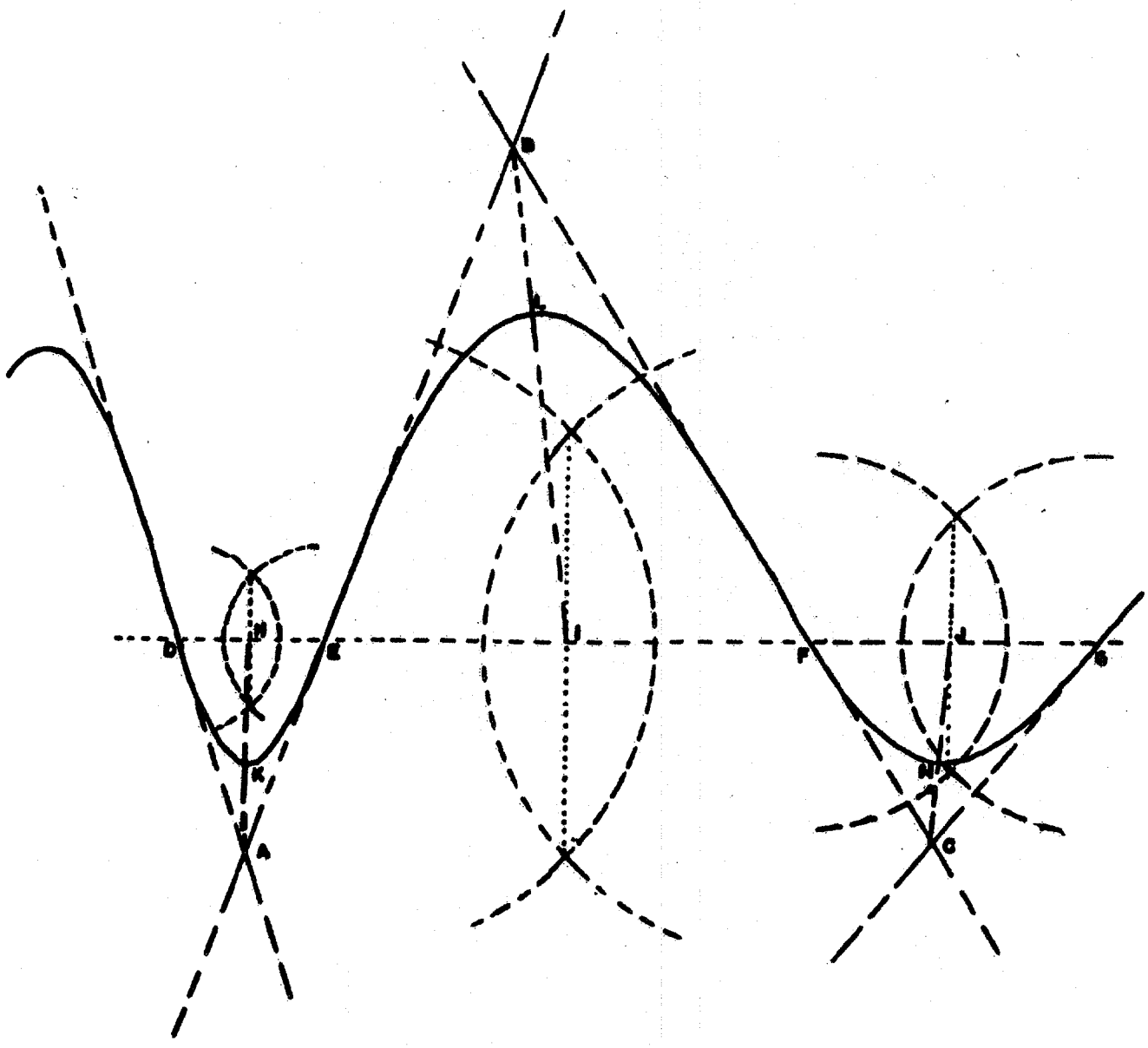

FIGURE IV- GEOMETRICAL LOCATION OF MAXIMA AND MINIMA

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TABLE I

DEPENDENCE OF RATE OF FILM LOSS ON INTENSITY OF IRRADIATION

WAVELENGTH	% OF FILM REMAINING	EXPOSURE TIME AT I_I	EXPOSURE TIME AT I_{II}	$TIME_I/TIME_{II}$
> 2000 Å	90%	20 hrs.	7 hrs.	2.9
	80	39	14	2.8
	70	59	21	2.8
	60	77	27	2.9
> 2500 Å	95%	25 hrs.	7 hrs.	3.5
	92	63	19	3.3
	88	142	44	3.2
> 2950 Å	98%	22 hrs.	8 hrs.	2.8
	96	54	20	2.7
	94	100	40	2.5
	92	148	52	2.8
> 3500 Å	99%	36 hrs.	16 hrs.	2.2
	98	81	35	2.3
	97	130	56	2.3

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TABLE 2 EFFECT OF WAVELENGTH ON RATE OF FILM LOSS

WAVELENGTH INTERVAL	TOTAL INCIDENT ENERGY	Å ERODED *	% ENERGY ABSORBED	Å ERODED/ MILLIWATT ABSORBED
2000–2500Å	.017 WATTS/CM	4705	100%	277
2500–2950Å	.009	573	50%	128
2950–3500Å	.003	352	30%	353
>3500Å	.017	220	5%	271

*OBTAINED FROM (TOTAL Å ERODED BY ALL WAVELENGTHS > LOWER LIMIT) MINUS (TOTÁL Å ERODED BY WAVELENGHTS > UPPER LIMIT)

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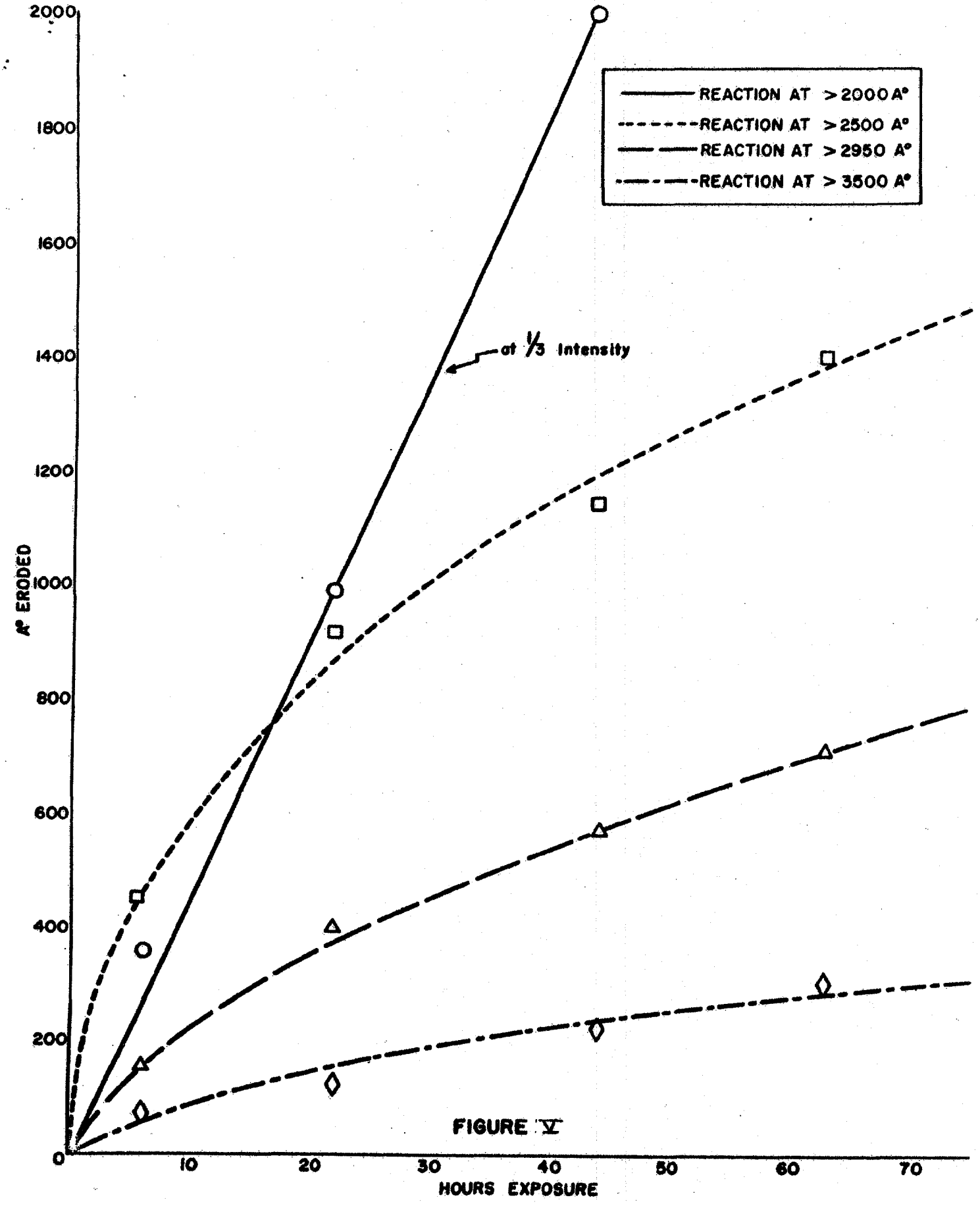

FIGURE V

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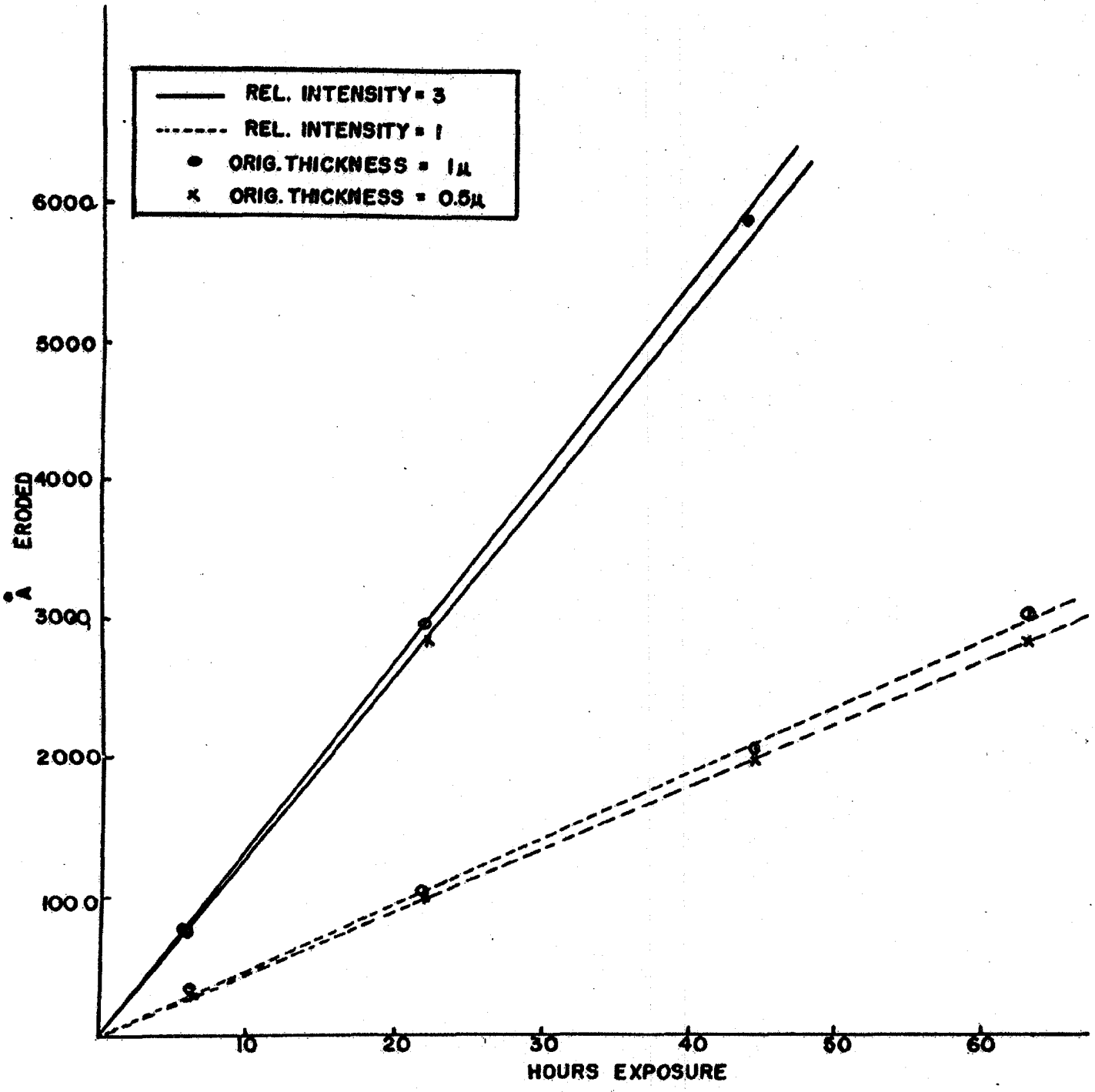

FIGURE XI - RATE OF FILM LOSS UNDER UNFILTERED LIGHT

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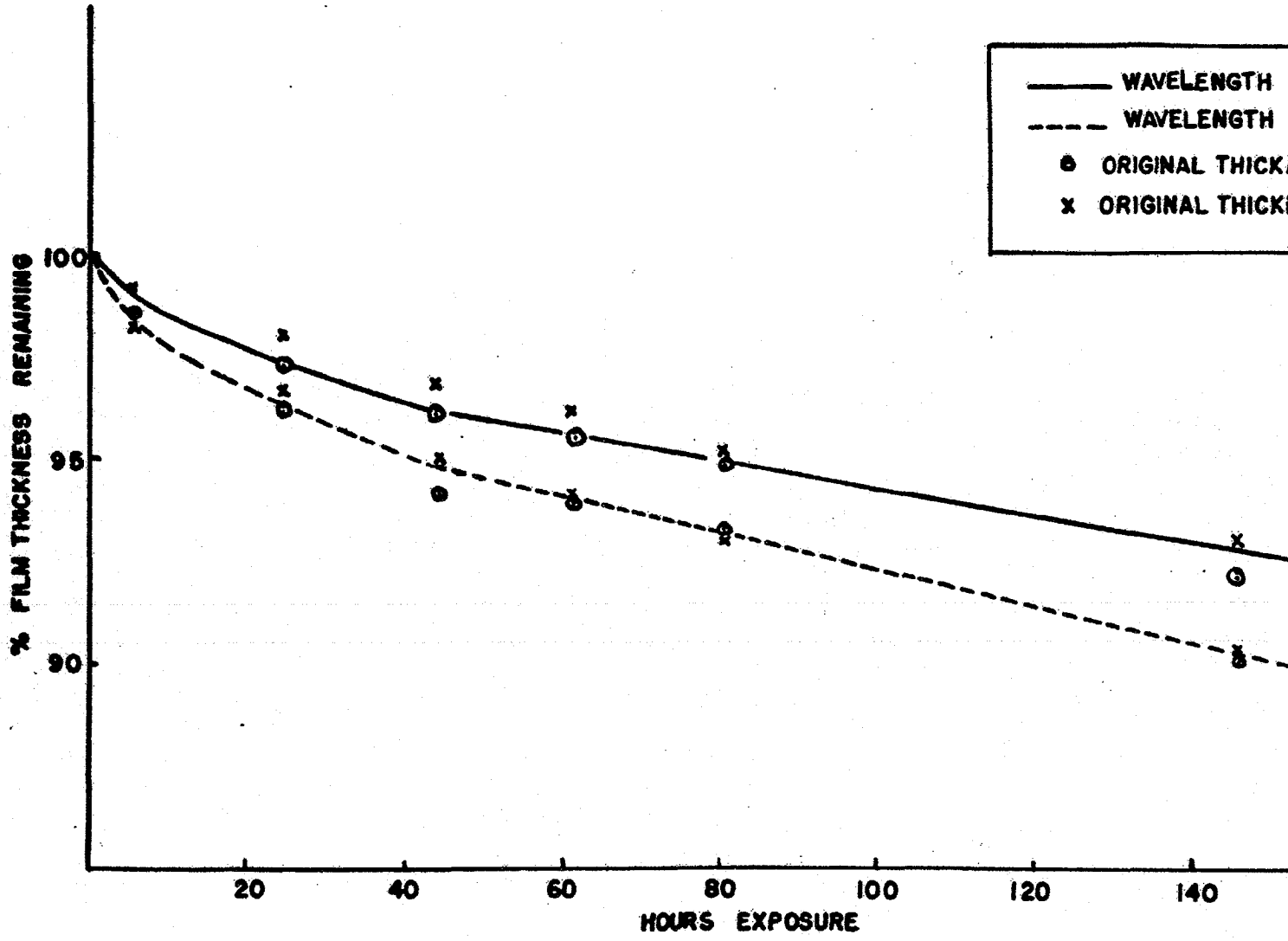

FIGURE VII— RATE OF FILM LOSS AT VARIOUS WAVELENGTH DISTRIBUTION

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TABLE III

CALCULATION OF FIRST ORDER RATE CONSTANT FOR FILM LOSS AT >2950 Å

$$\left(k = \frac{2.303}{t} \log \frac{a}{a-x} \right)$$

where a = original thickness

$a-x$ = thickness at time = t

TIME HRS.	FILM THICKNESS REMAINING	$k \times 10^3$
0	9160	
6	9000	2.66
22	8760	1.96
44	8580	1.46
63	8450	1.28
108	8130	1.13
128	8050	1.11
148	7970	1.10
165	7920	0.88

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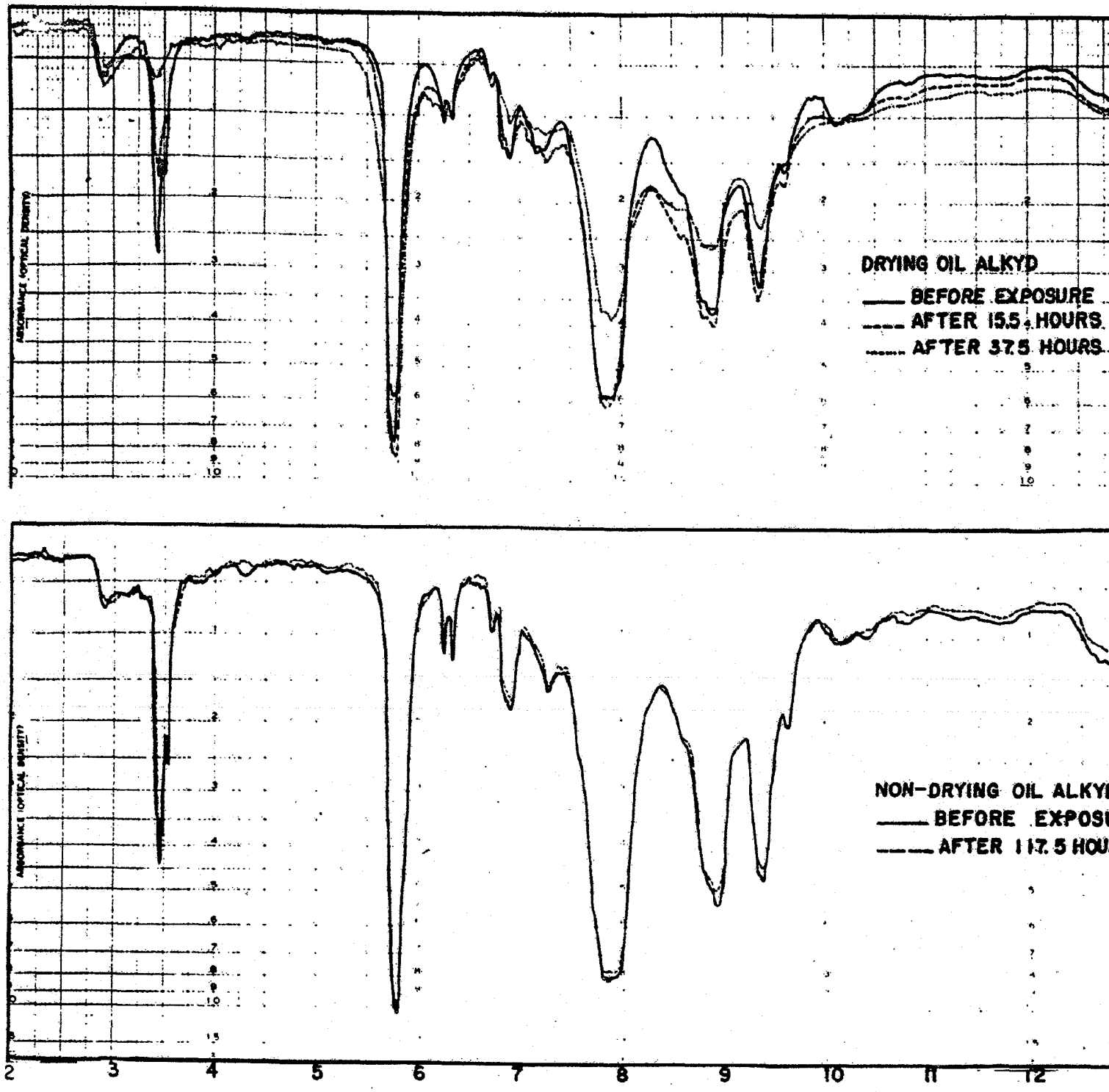

FIGURE VIII INFRARED SPECTRA OF ALKYD RESINS BEFORE AND AFTER IRRADIATION

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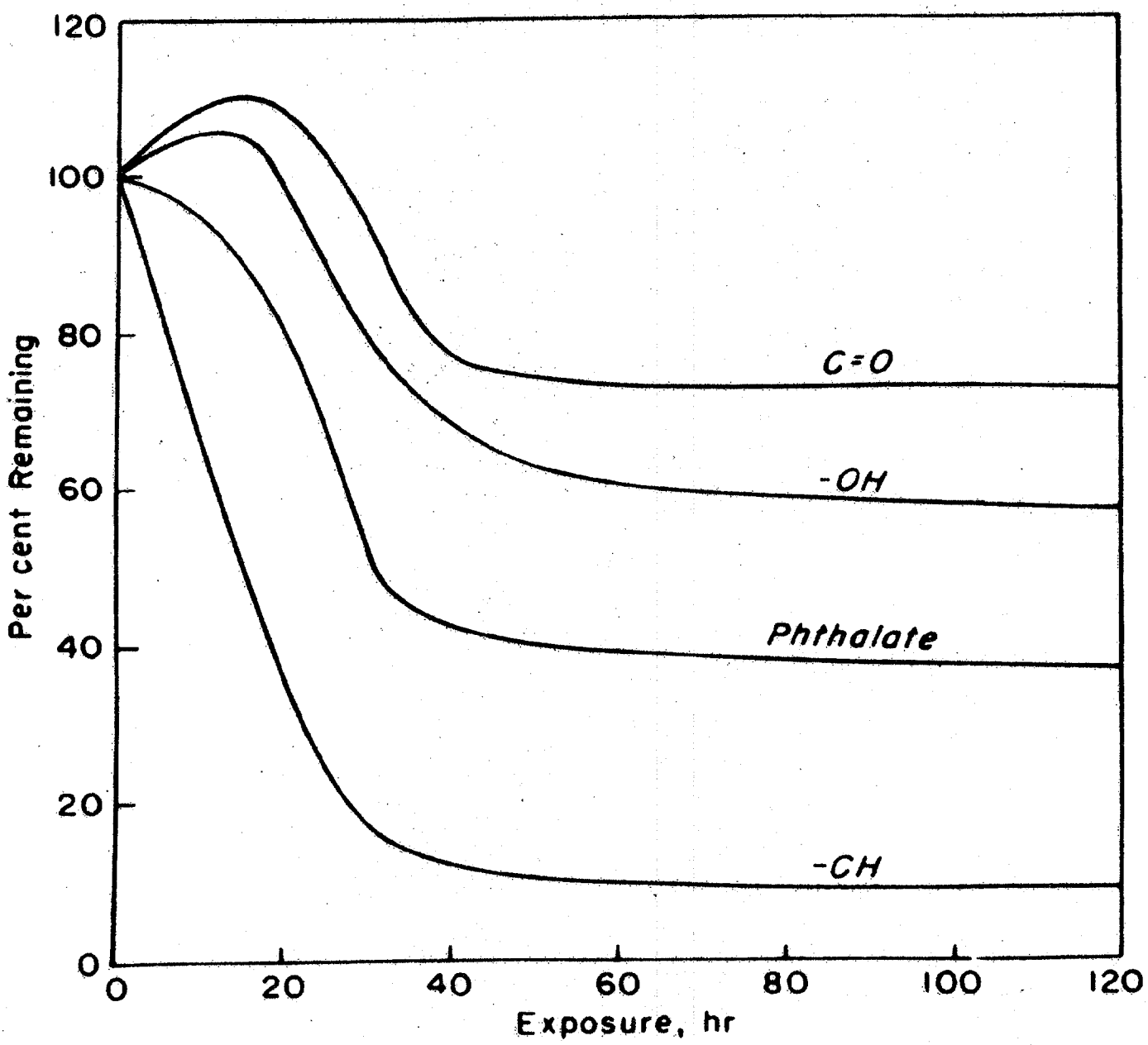

FIGURE IX. **Changes in Functional Group Concentrations Resulting from Exposure.**

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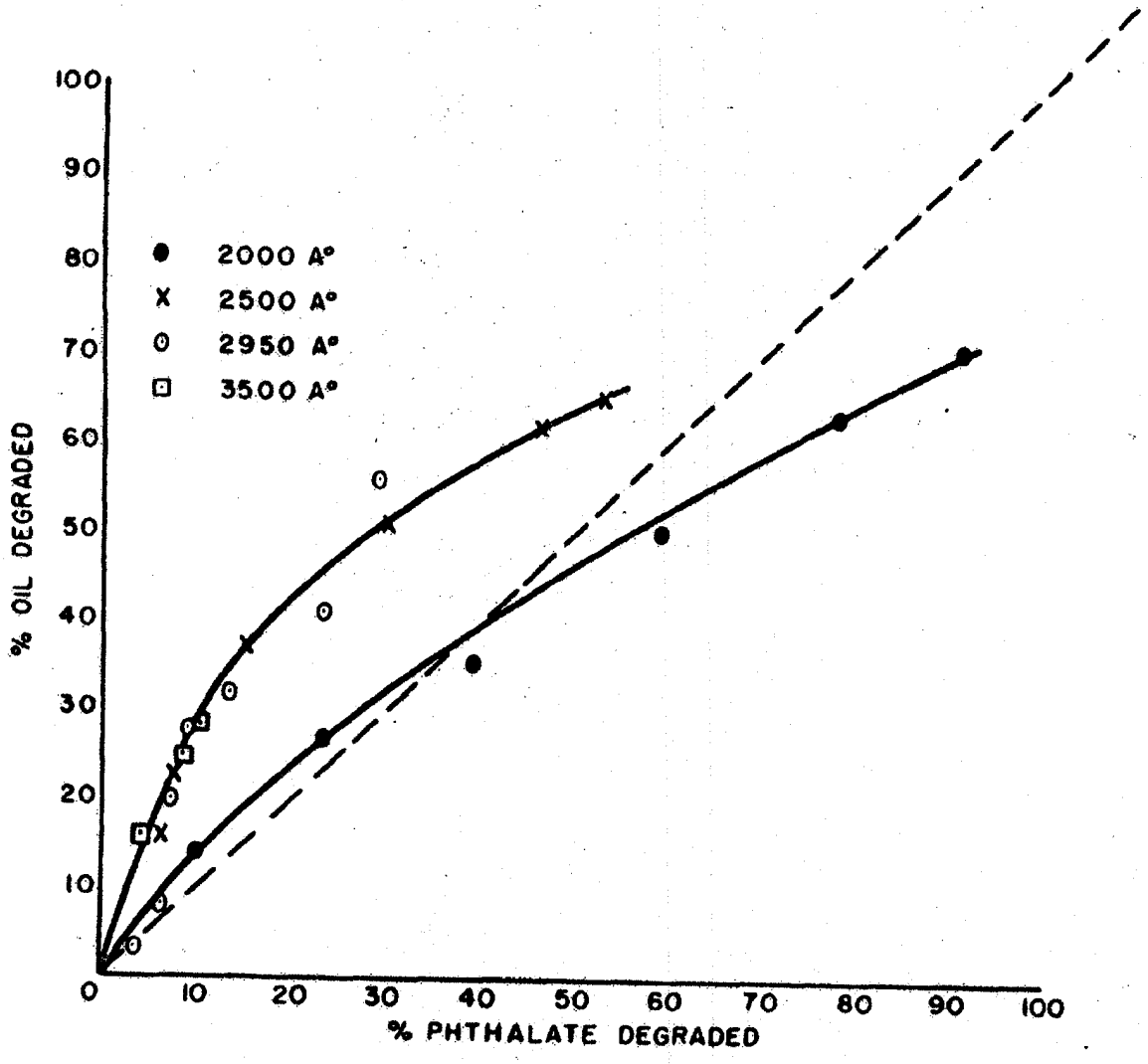

FIGURE X EFFECT OF WAVELENGTH ON ALKYD DEGRADATION

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