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Technical Memorandum TM 80551

ULTRAVIOLET ABSORPTION OF COMMON SPACECRAFT CONTAMINANTS

Joe A. Colony

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National Aeronautics and
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(NASA-TM-80551) ULTRAVIOLET ABSORPTION OF COMMON SPACECRAFT CONTAMINANTS (NASA) 28 p HC A03/MF A01 CSCL 20F
N79-34015
Unclas
G3/74 38905

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ABSTRACT

Organic contamination on ultraviolet optical systems can degrade the signal by reflection, scattering, interference, and absorption. The first three processes depend on the physical state of the contaminant while absorption depends on its chemical structure. The latter phenomenon was isolated from the others by dissolving contaminants in cyclohexane and determining absorption spectra from 2100A to 3600A. A variety of materials representing the types of contaminants responsible for most space flight hardware problems was scanned and the spectra are included in this report. In addition, the effect of thickness was demonstrated for the most common contaminant, di(2-ethyl hexyl)phthalate, by scanning successive dilutions. This collection of spectral data should provide some insight into the problems of predicting the extent and nature of contaminant-induced degradation of the performance of ultraviolet instruments during both test and actual space flight.

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ULTRAVIOLET ABSORPTION OF COMMON SPACECRAFT CONTAMINANTS

I. INTRODUCTION

As a result of the development of sensitive ultraviolet experiments, the importance of optical contamination has become critical. To illustrate the magnitude of the problem, an experimenter on the ESTEC TD-1A ultraviolet astronomy experiment (S 2/68) has stated that as little as 25 angstroms of condensate on the optical surfaces could substantially degrade their reflectance and impair the equipment.[1] The total optical efficiency of the system was required to be at least 60% of the calibration value which meant that reflectance losses of 10% on each of the five optical surfaces could not be tolerated. This experiment (S 2/68) employed ultraviolet wavelengths of 1300-3000 Å which is approximately the same range as for the IUE Spacecraft which has two cameras – camera 1 = 1190-1920 Å and camera 2 = 1830-3080 Å.

Any study of the effects of contamination on optical systems becomes a multi-faceted problem. To begin with, attenuation of an optical signal can be caused by any or all of four phenomena, namely, reflection, scattering, interference, and absorption. The first three of these are physical processes and depend primarily on properties such as thickness of contaminant, refractive index, particle or droplet size and concentration, and angle of incidence of the optical signal. Absorptance, however, is determined by the chemical structure of the contaminant. Thus, an absorptance spectrum over the wavelength of the experiment would be required in order to evaluate the effect of each contaminant.

The problem of conducting meaningful tests to evaluate effects of contaminants is often compounded by interactions and synergistic effects between the four types of attenuating phenomena. For example, it has been shown that the amplitude of the interference fringe absorption of an evaporated coating composite (SiO_x over vapor deposited aluminum) is sharply increased by the addition of a very thin (20A) layer of carbon.[2] In another test it was shown that loss of reflectance of a magnesium fluoride coated aluminum mirror was drastic at 1216 A due to scattering caused by diffusion pump oil (DC 705) in droplet form. An equivalent thickness of 85 A caused a reflectance loss of over 50% and, moreover, subsequent ultraviolet irradiation increased this loss to over 90% and made it permanent.[2] This large effect of loss due to scattering has been cited as a reason for discontinuing a project at GSFC illustrating the absorption characteristics of pump oils (DC 704, DC 705, and Octoil).[3] However, it must be realized that the factors determining the physical structure of a contaminant layer (droplets vs continous film) are complex and include chemical parameters of both the contaminant and the surface, temperature, and mode of deposition of the contaminant. Droplet formation is by no means universal and should not preclude the use of optical absorption data. In another program which attempted to evaluate the effects of contaminants outgassed from Apollo telescope mount materials, platinum mirrors were exposed to the outgassing products and measured at very short wavelengths (304 A, 584 A, and 1216 A).[4] The results were somewhat inconclusive, perhaps because of the fact that the initial reflectances of the mirrors were quite low (mostly less than 20%) and only small changes could be expected.

The results of these various experiences indicate that testing needs to be done and data made available on optical absorption of contaminant species in the ultraviolet region as well as on scattering, interference, and reflectance phenomena. This paper is an attempt to deal with one aspect of this problem, namely, optical absorption of common spacecraft contaminants. The selected list of contaminants was chosen as a result of several years' experience in this laboratory in analyzing contaminants from the various spacecraft built and tested by GSFC. These materials represent the types of materials which are the culprits in 80-90% of the problems actually incurred.[5] Specifically, the data presented in this report includes transmission spectra from 2000 A to 3600 A for these compounds. The spectra were obtained from solutions using a solvent which is transparent through this spectral region (spectro-grade cyclohexane). This procedure eliminates contributions from the other types of possible attenuating processes. Data for all materials was obtained at equal concentration in order to allow comparison of relative effect between various compounds. In addition, a series of dilutions for the most abundant plasticizer, di-(2-ethyl hexyl) phthalate was included to show the effect of contaminant thickness.

II. EXPERIMENTAL PROCEDURE

Cyclohexane was chosen as the solvent for the contaminants primarily because of the fact that it exhibited no absorption throughout the region of interest and because all of the contaminants were sufficiently soluble to allow the measurements to be made. The spectroanalyzed grade from Burdick and Jackson was used effectively as received. However, it was found to be imperative that the cleanliness of the quartz sample cuvettes be assured each time by running a spectral scan as a blank. It was often found to be necessary to rinse the cuvettes with fresh cyclohexane as many as ten or twelve times. Measurements were made using a Beckman DK-2A Spectrophotometer over the wavelength range 360 nm to 210 nm.

The concentration of contaminant was equal on a volume/volume basis for each sample and was chosen at a high level in order to vividly illustrate the positions of the various absorption bands. The following relationships were derived for the concentration factor and equivalent thickness of contaminant:

Amount added to cuvette - - - - - - - - - 0.5 ul $= 5 \times 10^{-4}$ cm^3

Cross sectional area of curvette - - - - - - - - - - 3.15 cm^2

Then the thickness $= 5 \times 10^{-4}\ \text{cm}^3/3.15\ \text{cm}^2 = 1.58 \times 10^{-4}$ cm

$= 1.58$ microns

$= \underline{1.58 \times 10^{4}\ \text{A}}$

If the density is assumed to be lg/cm^3

Then the weight per unit area is calculated;

$0.5\ \text{ul} = 5 \times 10^{-4}$ ml

$= 5 \times 10^{-4}$ cm^3

and $5 \times 10^{-4}\ \text{cm}^3 \times \text{lg/cm}^3 = 5 \times 10^{-4}$ g

$= 500$ ug

so $500\ \text{ug}/3.15\ \text{cm}^2 = \underline{158\ \text{ug/cm}^2}$

The same type of calculation was used to prepare a stock solution of the most common plasticizer, di (2-ethyl hexyl)phthalate (DEHP). From this stock solution a series of known dilutions was made and spectra obtained to show the effect of thickness on absorptance.

The stock solution contained 31.5 g DEHP/1 = 31.5×10^{-6} g/ul

Then 1 ul of stock solution added to the cuvette with a surface area

of 3.15 cm^2 was equivalent to 10 ug/cm^2.

$$31.5 \times 10^{-6}\ g/3.15\ cm^2 = 10\ ug/cm^2$$

by calculation above - - - - - = 1000 A thickness

A list of the materials included in this study and their experimentally obtained absorption spectra are presented as an appendix to this report.

III. DISCUSSION AND CONCLUSIONS

Observation of the spectra of these individual spacecraft contaminants illustrates the complexity and variety of absorption patterns which is possible. Of course, in the real world, a combination of materials and proportions will determine the ultimate spectral effect on any given optical system.

Tentatively, some generalized conclusions relating the observed absorption characteristics to chemical structures can be made. None of these relatively pure contaminants shows appreciable absorption above 3000A and, in fact, all are nonabsorbing in the visible region. However, between 3000 and 2000A *all* compounds which include an aromatic ring structure become *strongly* absorbing. This group includes some of the most commonly encountered materials such as di(2-ethyl hexyl) phthalate (DEHP), DC 704 diffusion pump oil, BHT antioxidant, and TCP oil additive and fire retardant. Most other materials also become somewhat absorbing in this region with sharp absorption edges below 2500A associated with carbonyl functions and less dramatic absorption due to unsaturation in aliphatic hydrocarbons. Except for pure methyl silicones and perfluorinated oils, which showed no absorption at all, it appears that very strong effects might be expected from most contaminants at wavelengths shorter than 2000A.

In addition to the effects measured and exhibited here, it should be remembered that the process of solarization (degradation due to ultraviolet radiation) can cause dramatic optical changes in a contaminant film. Under the influence of such exposure, contaminants can become irreversibly bound to an optical surface and even methyl silicones can acquire absorption bands throughout the ultraviolet and into the visible region.

The presentation of this data should provide some insight into the extent and nature of degradation of optical signals in ultraviolet instruments in space due to absorption by organic contaminants. It is hoped that it might be useful in predicting effects and possibly as an aid in explanation or clarification of degradation which has already occurred in flight. In any event, it shows that any such attempts at prediction would require extensive knowledge concerning the amounts and types of contamination as well as its physical state on the surface.

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4. Final Report; "Test Program on the Contamination of Ultraviolet-Region Mirrors by Apollo Telescope Mount Materials F74-01" January 14, 1974. Prepared for NASA, MSFC, Contract NAS8-27996.

5. Colony, J. A., "Mass Spectrometry of Aerospace Materials," NASA TN D-8261, June, 1976.

APPENDIX

LIST OF ULTRAVIOLET ABSORPTION SPECTRA

I. Materials at Equivalent Thickness (1.58×10^4 A)

1. Krytox 143 AB – Fluorinated Oil
2. RTV-11 Methyl Silicone
3. Polychlorinated Biphenyls (PCB)
4. 2, 6 di tertiary butyl p-cresol (BHT) – anti oxidant
5. Santovac 5 Polyphenyl Ether – diffusion pump oil
6. DC 704 Methyl Phenyl Silicone – diffusion pump oil
7. Duo Seal Pump Oil – mechanical pump oil
8. Apiezon C – hydrocarbon oil
9. Tricresyl Phosphate (TCP)
10. Butyl Stearate
11. DC 200 Methyl Silicone Oil (3.0 cp.)
12. Methyl Methacrylate – acrylic ester
13. Vinyl Acetate – aliphatic ester
14. P-10 Oil, di (2 ethyl hexyl) sebacate
15. Di (2-ethyl hexyl) phthalate (DEHP) – plasticizer

II. The Effect of Thickness on Ultraviolet Absorption

16. Di (2 ethyl hexyl) phthalate – 1000A-25,000A

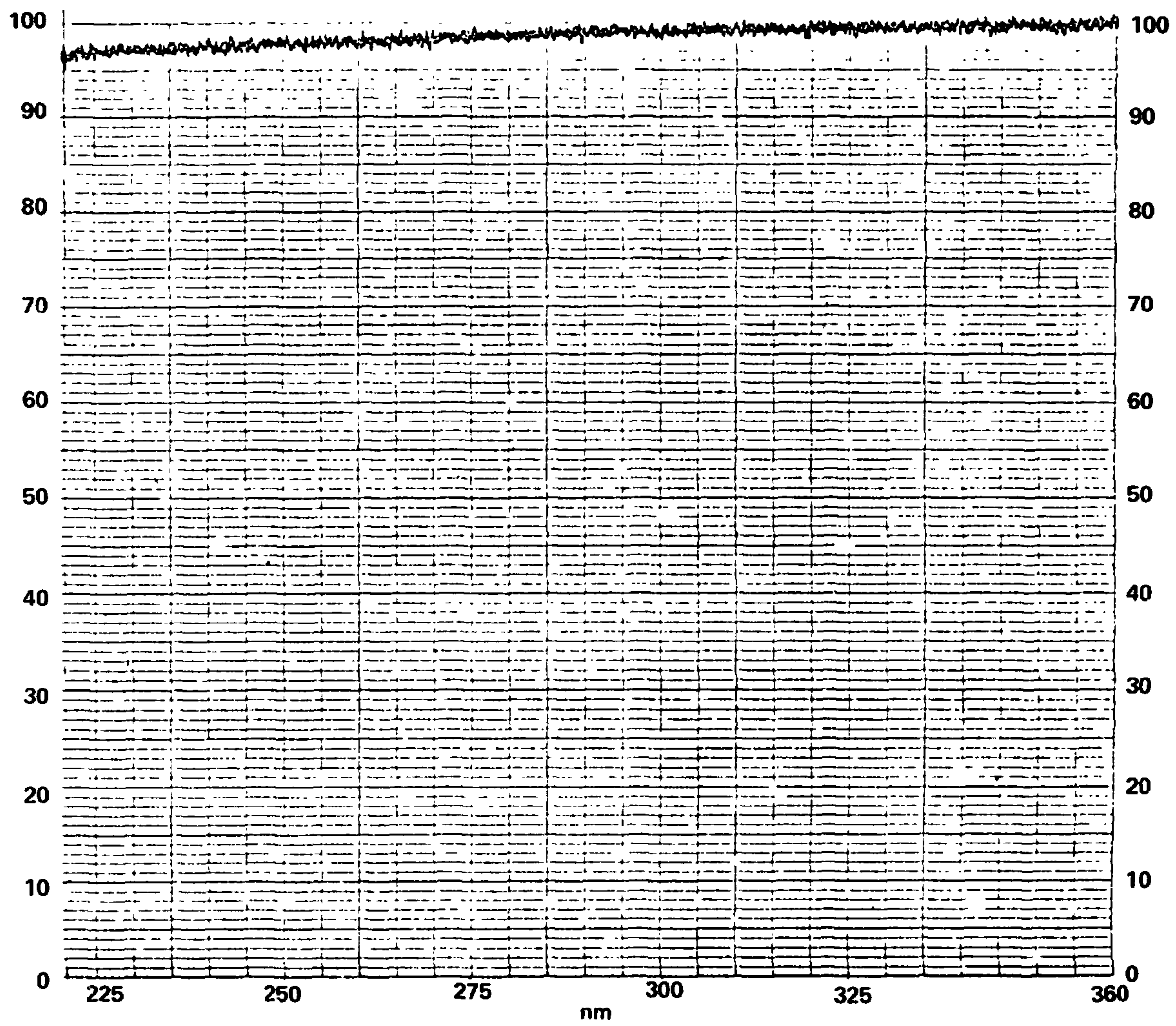

Figure .. vtox 143 AB – Fluorinated Oil
ivalent Thickness 1.58 × 10^4 A

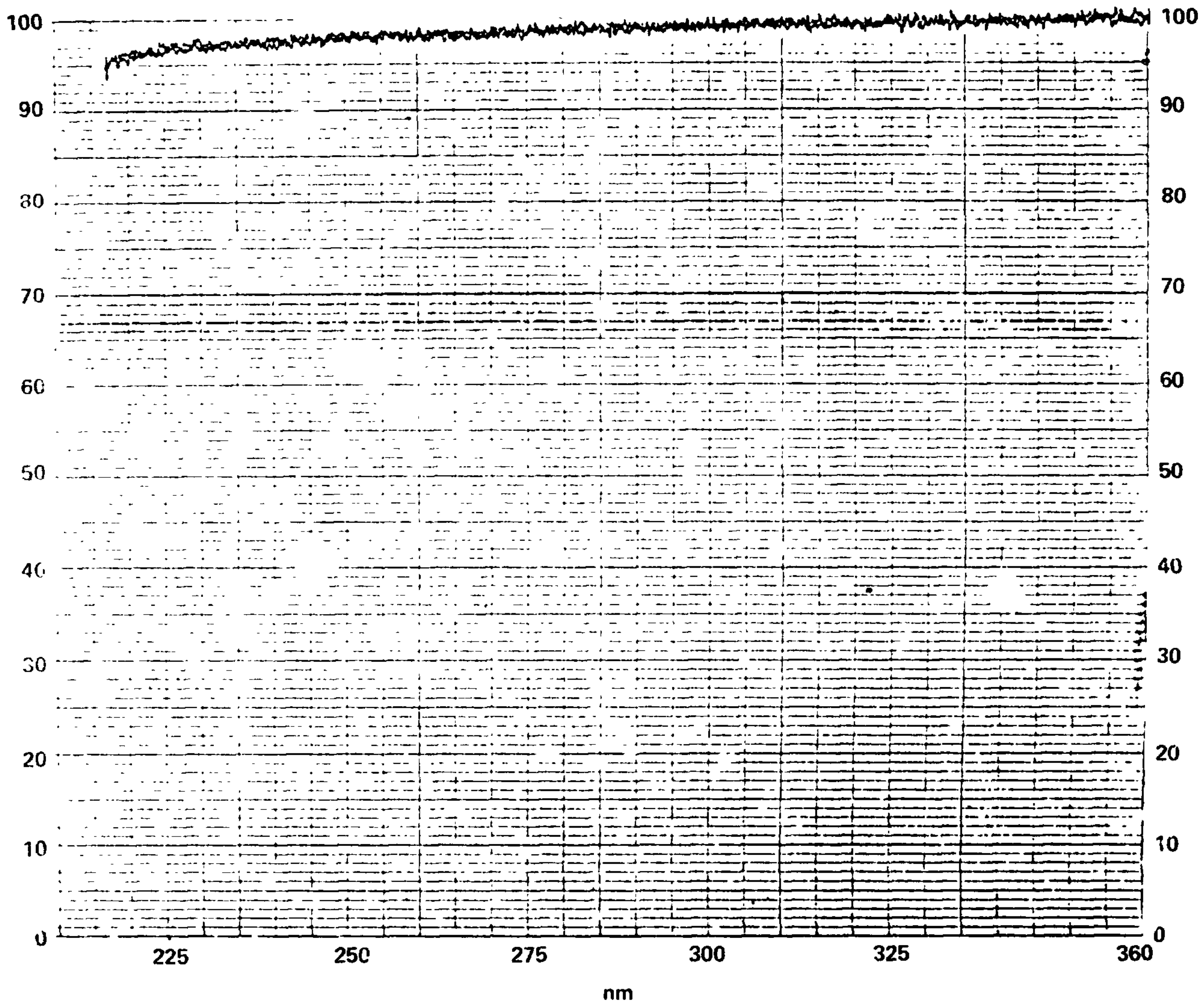

Figure 2. RTV-11 Methyl Silicone
Equivalent Thickness 1.58×10^4 A

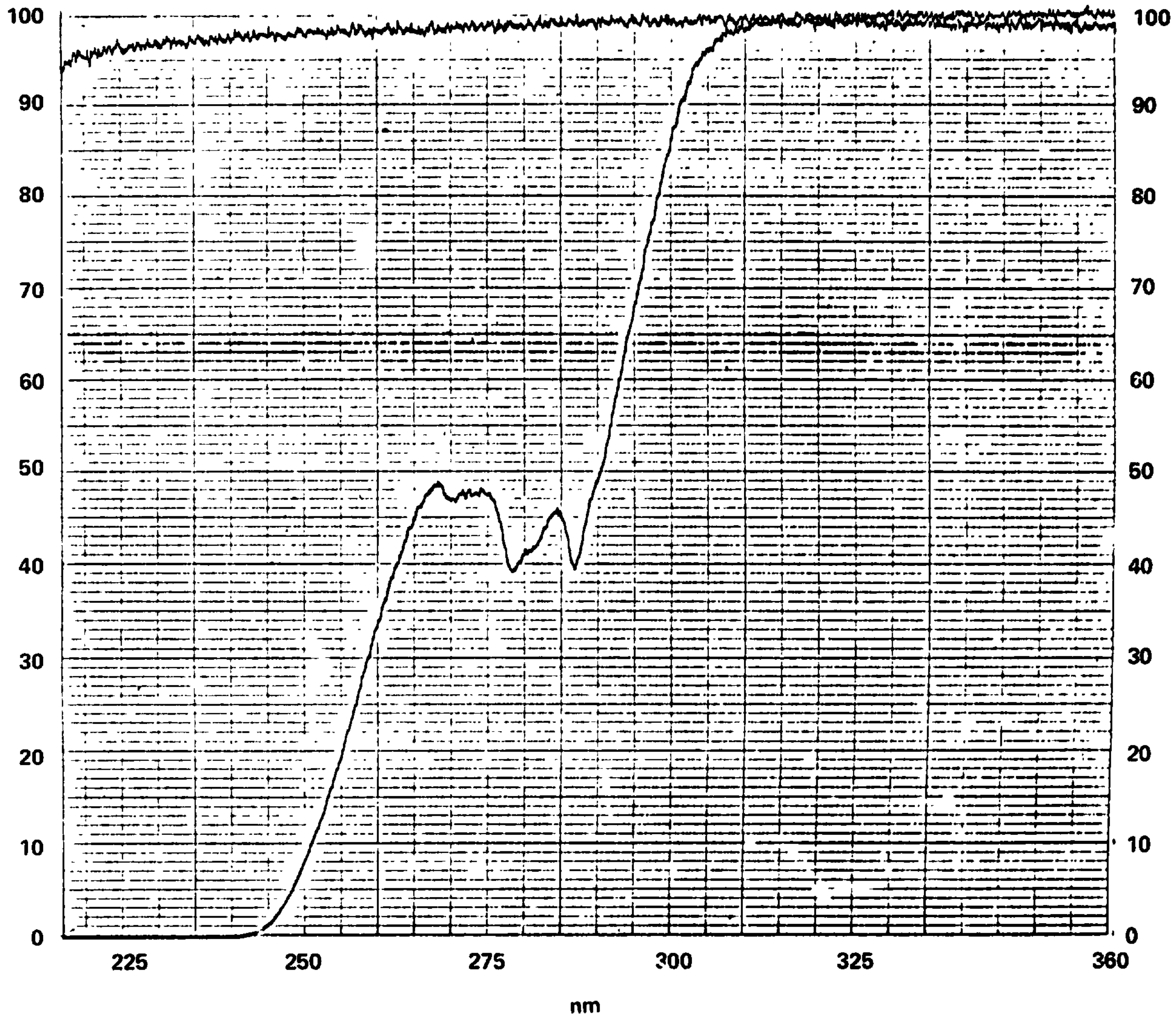

Figure 3. Polychlorinated Biphenyls (PCB)
Equivalent Thickness 1.58 × 10^4 A

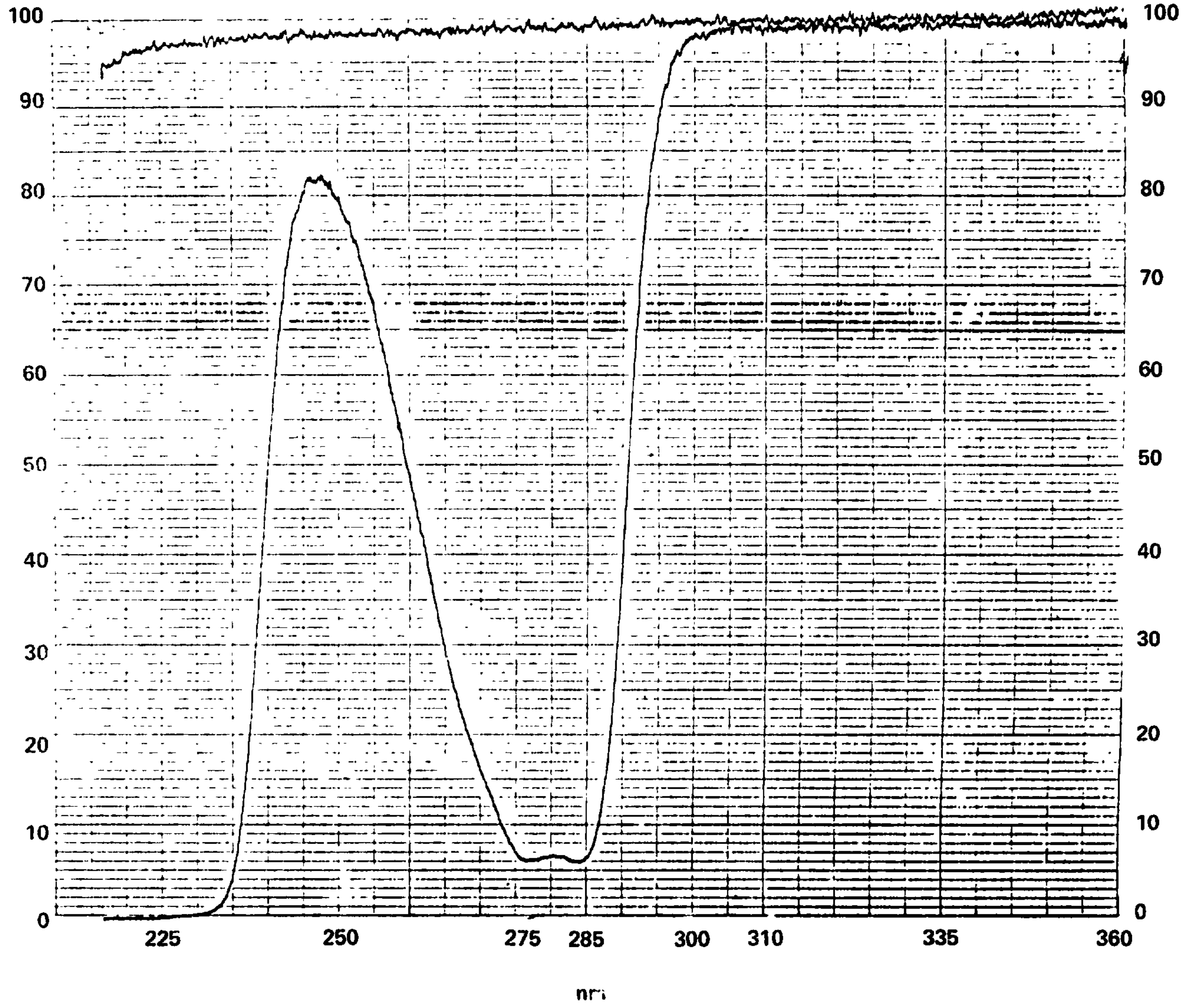

Figure 4. 2, 6 ditertiary butyl p-cresol (BHT) – anti oxidant
Equivalent Thickness 1.58 X 10^4 A

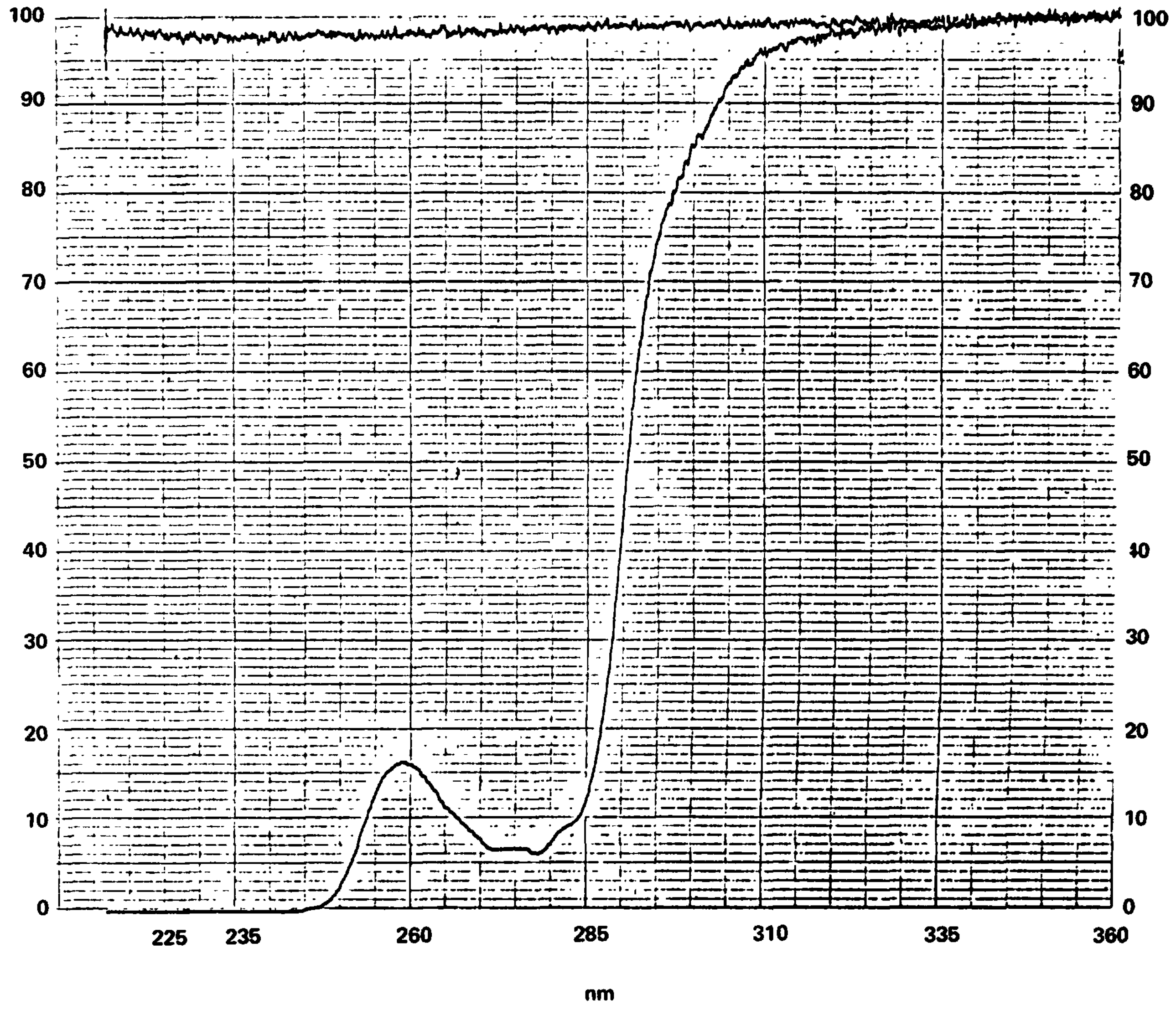

Figure 5. Santovac 5 Polyphenyl Ether – diffusion pump oil
Equivalent Thickness 1.58 × 10^4 A

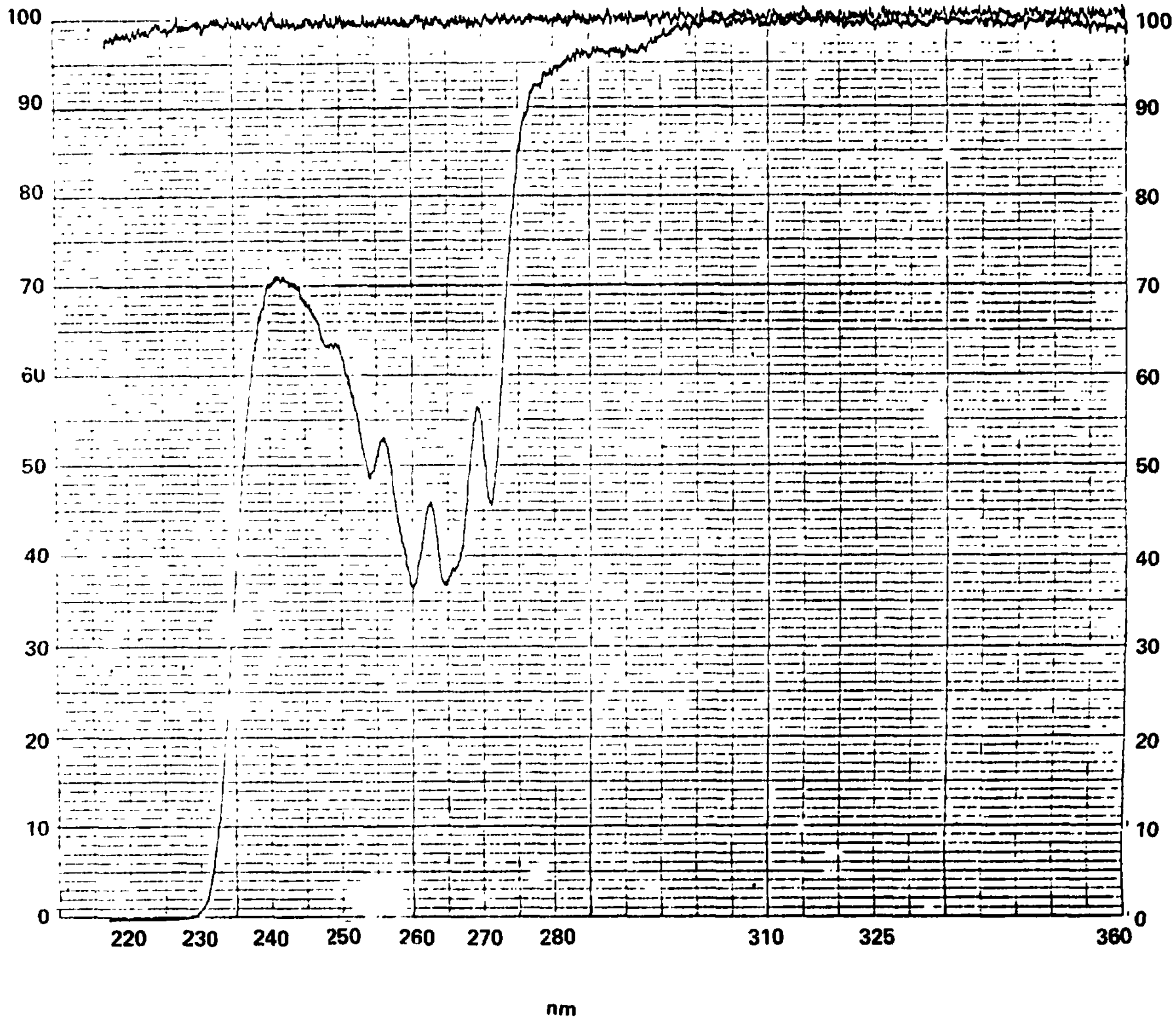

Figure 6. DC 704 Methyl Phenyl Silicone – diffusion pump oil
Equivalent Thickness 1.58 × 10^4 A

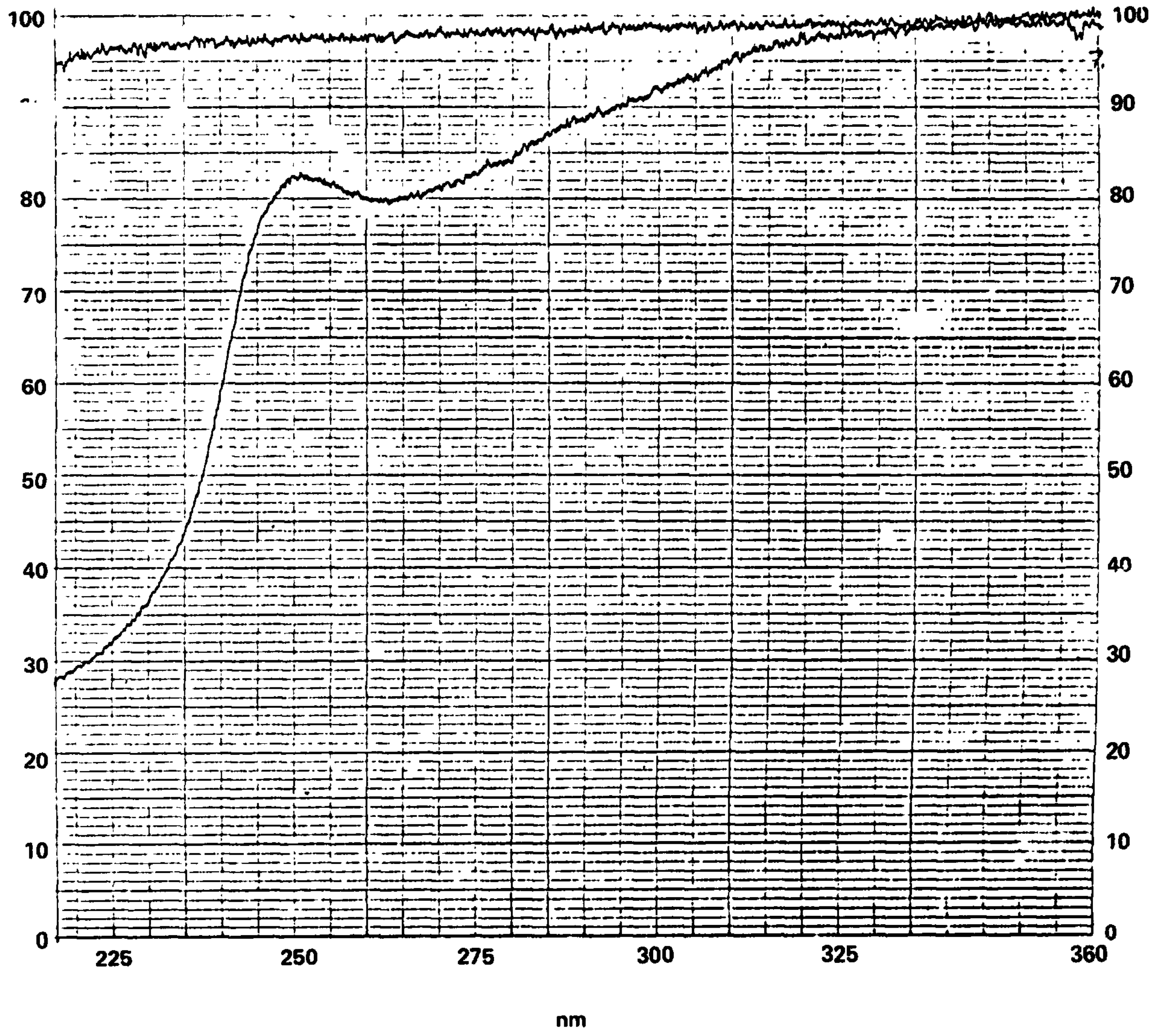

Figure 7. Duo Seal Pump Oil – mechanical pump oil
Equivalent Thickness 1.58 × 10^4 A

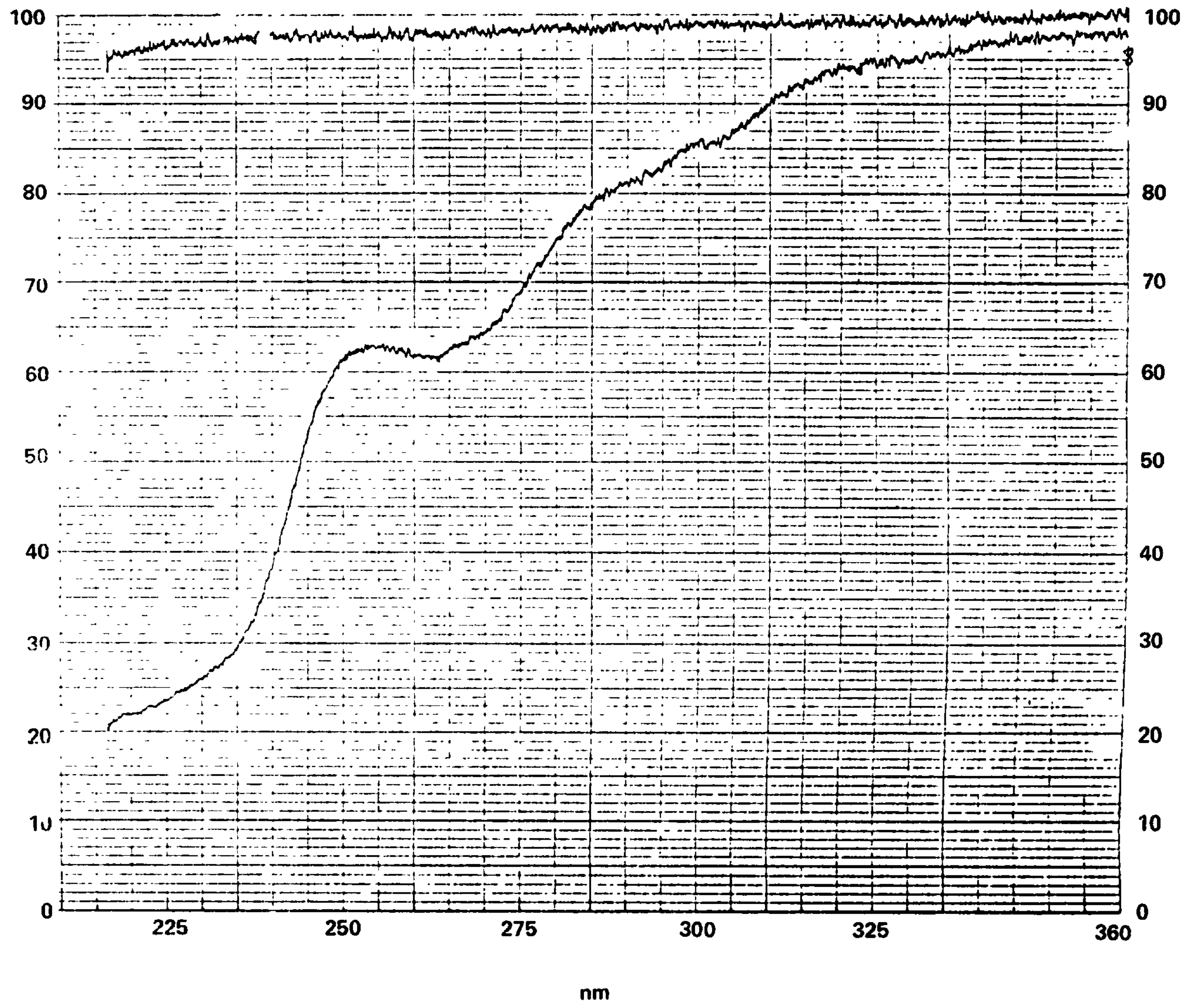

Figure 8. Apiezon C – hydrocarbon oil
Equivalent Thickness 1.58 X 10^4 A

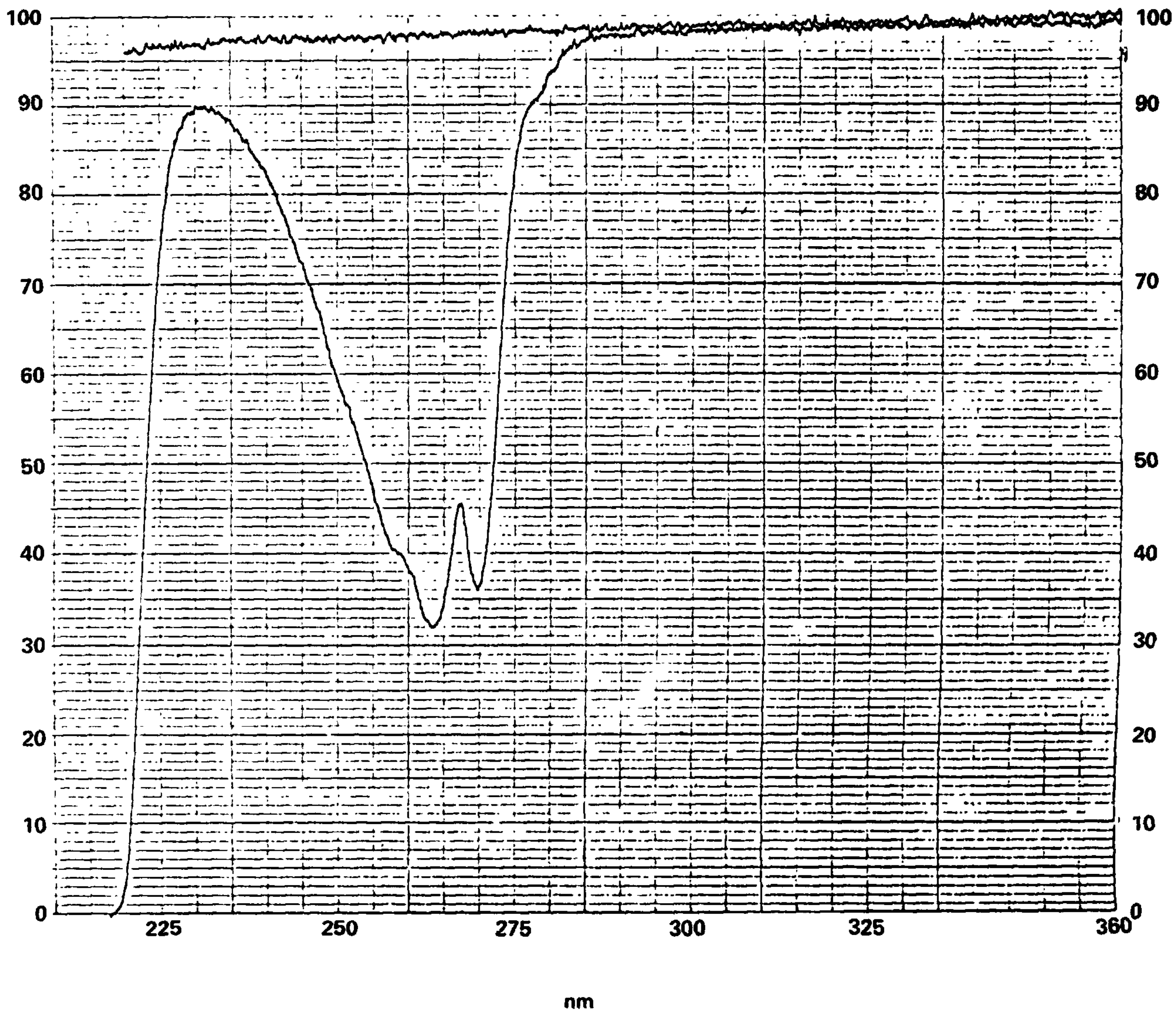

Figure 9. Tricresyl Phosphate (TCP)
Equivalent Thickness 1.58 × 10^4 A

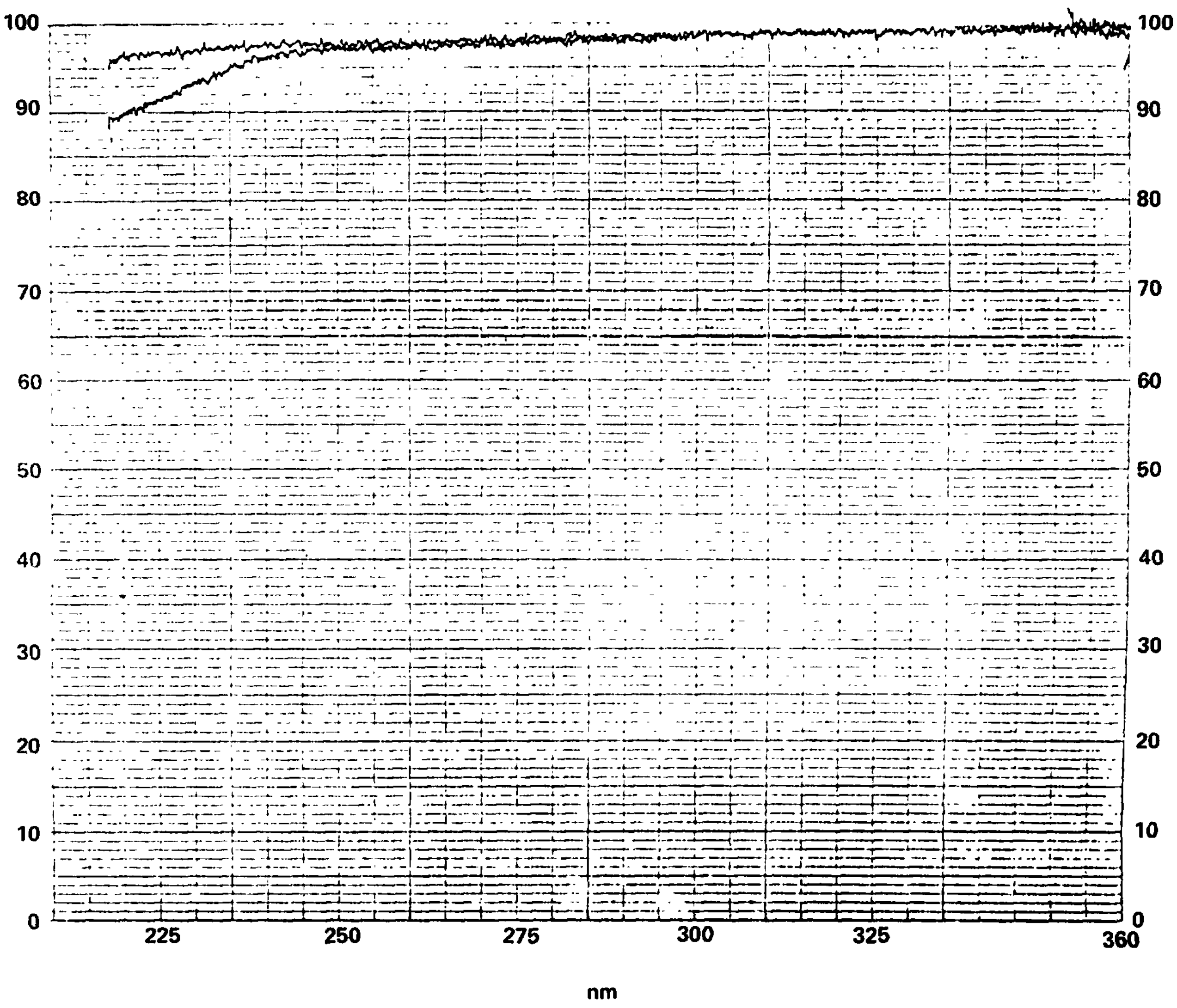

Figure 10. Butyl Stearate
Equivalent Thickness 1.58×10^4 A

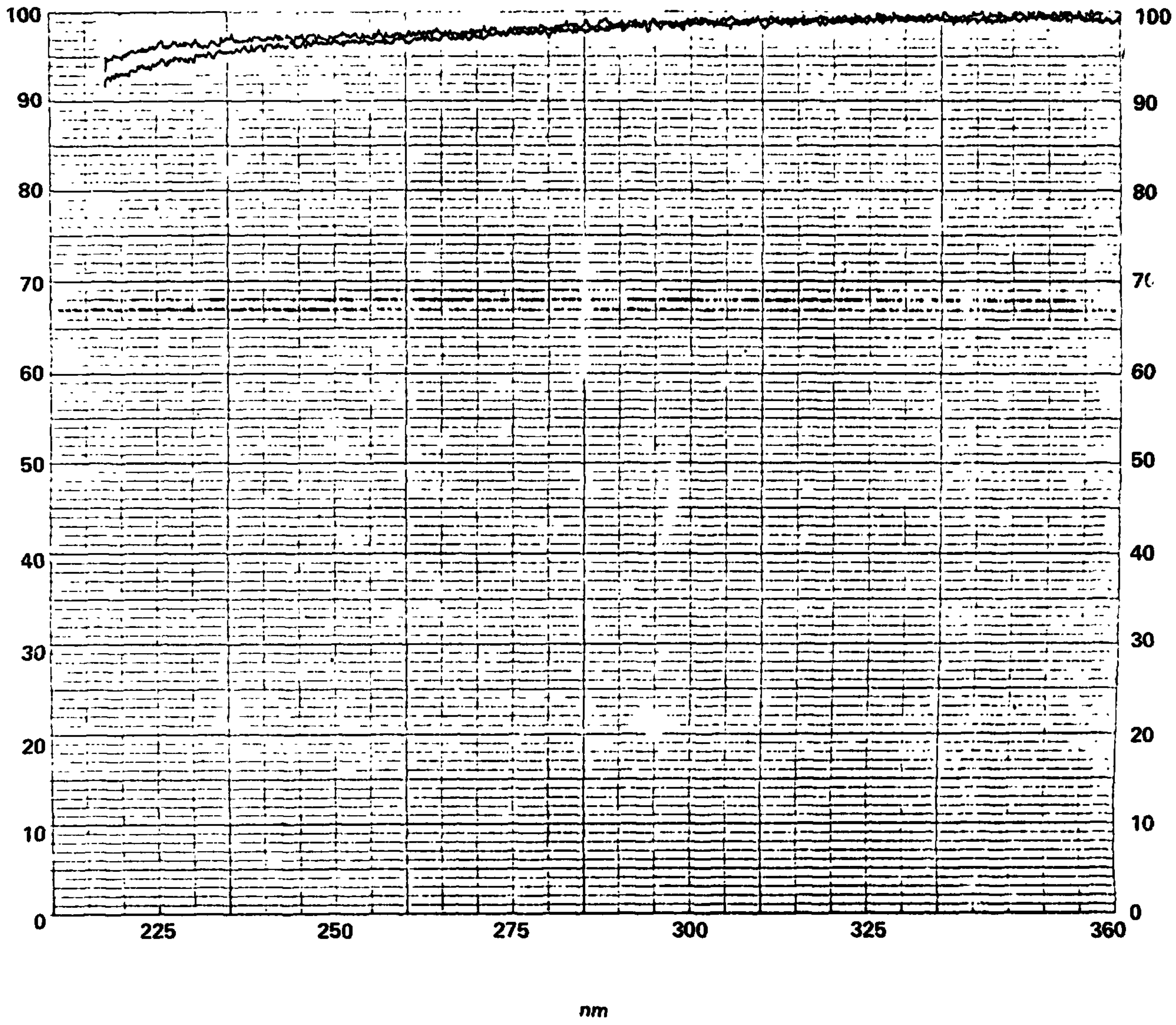

Figure 11. DC 200 Methyl Silicone Oil (3.0 op.)
Equivalent Thickness 1.58 × 10^4 A

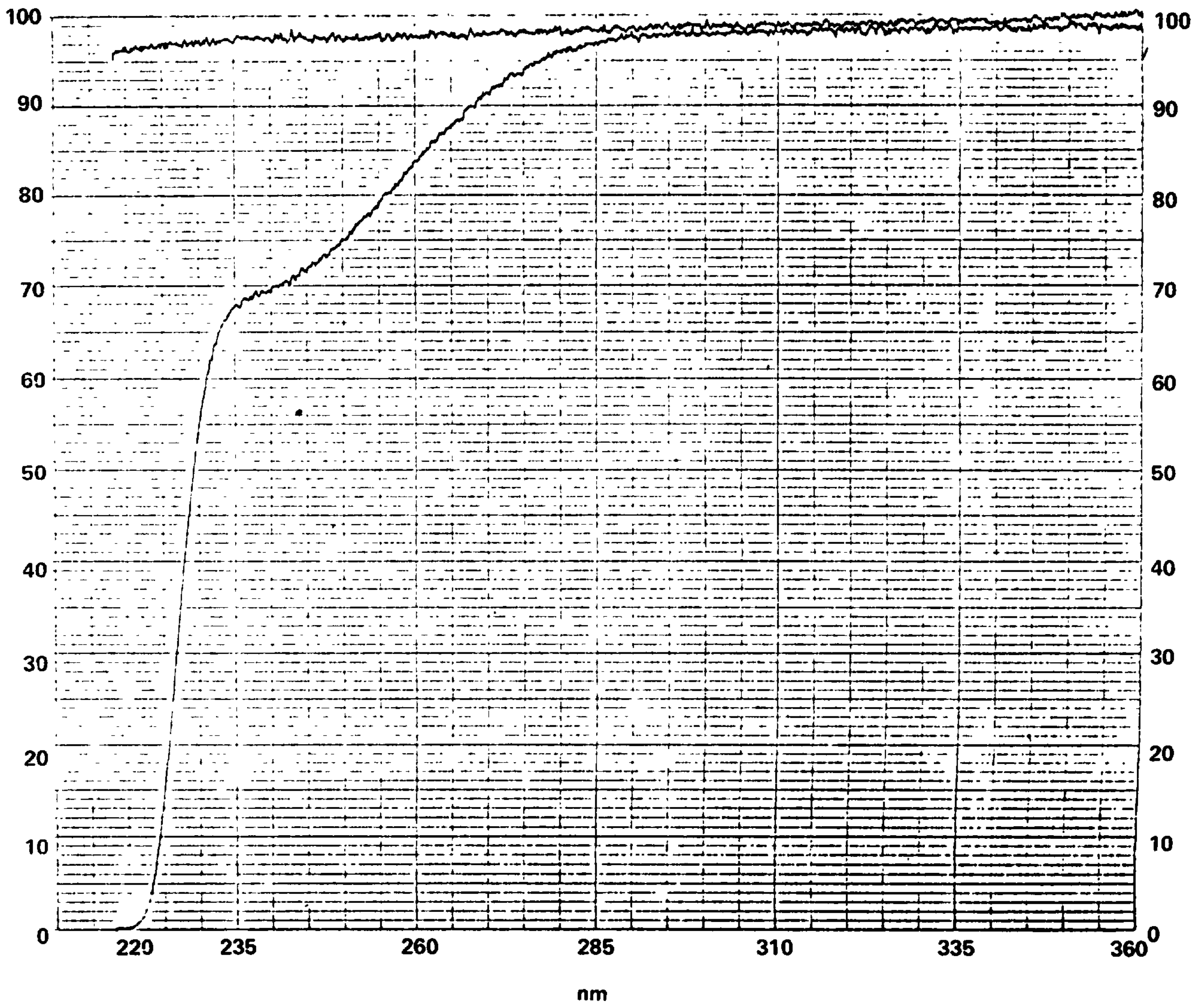

Figure 12. Methyl Methacrylate – acrylic ester
Equivalent Thickness 1.58 × 10^4 A

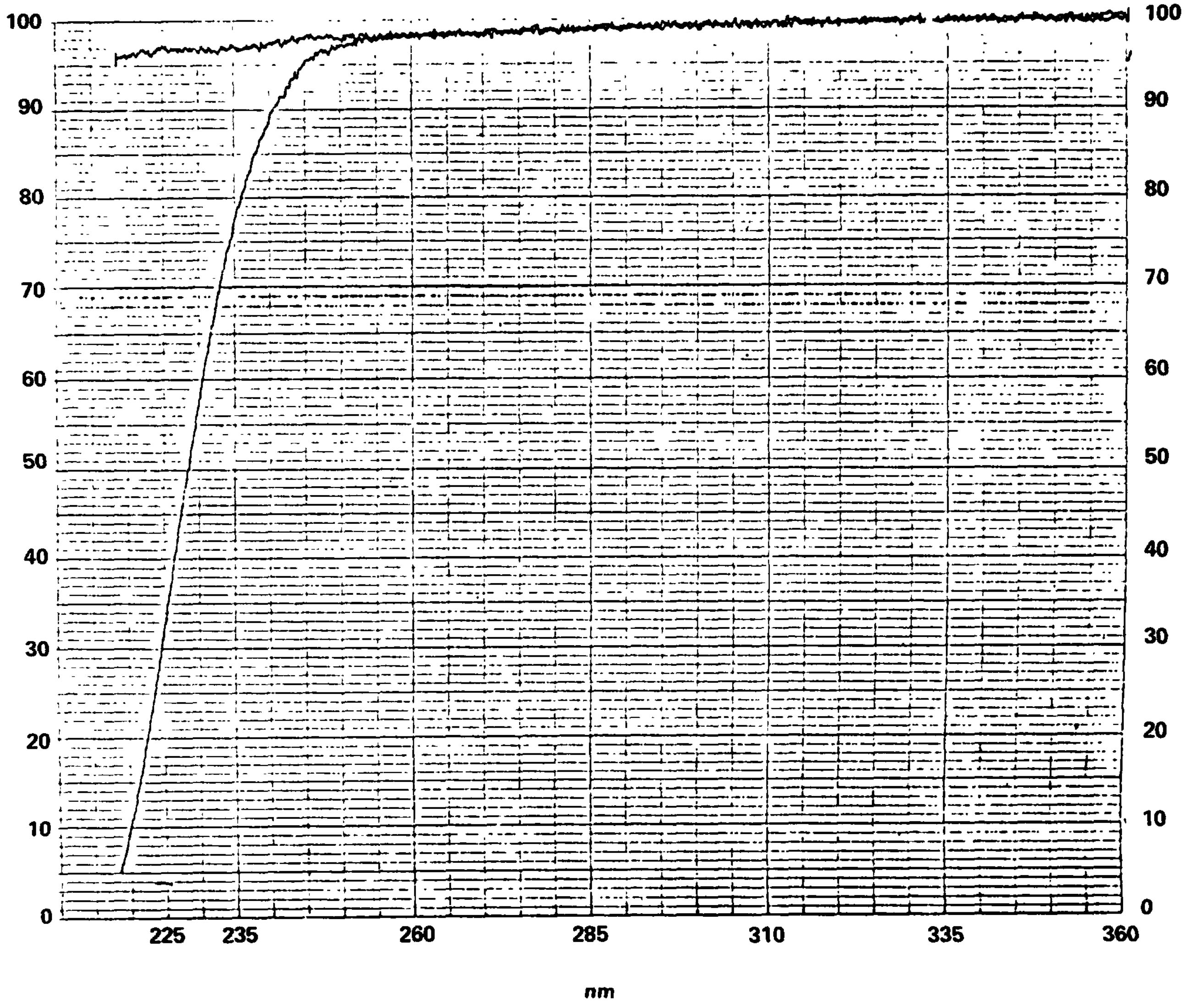

Figure 13. Vinyl Acetate – aliphatic ester
Equivalent Thickness 1.58 X 10^4 A

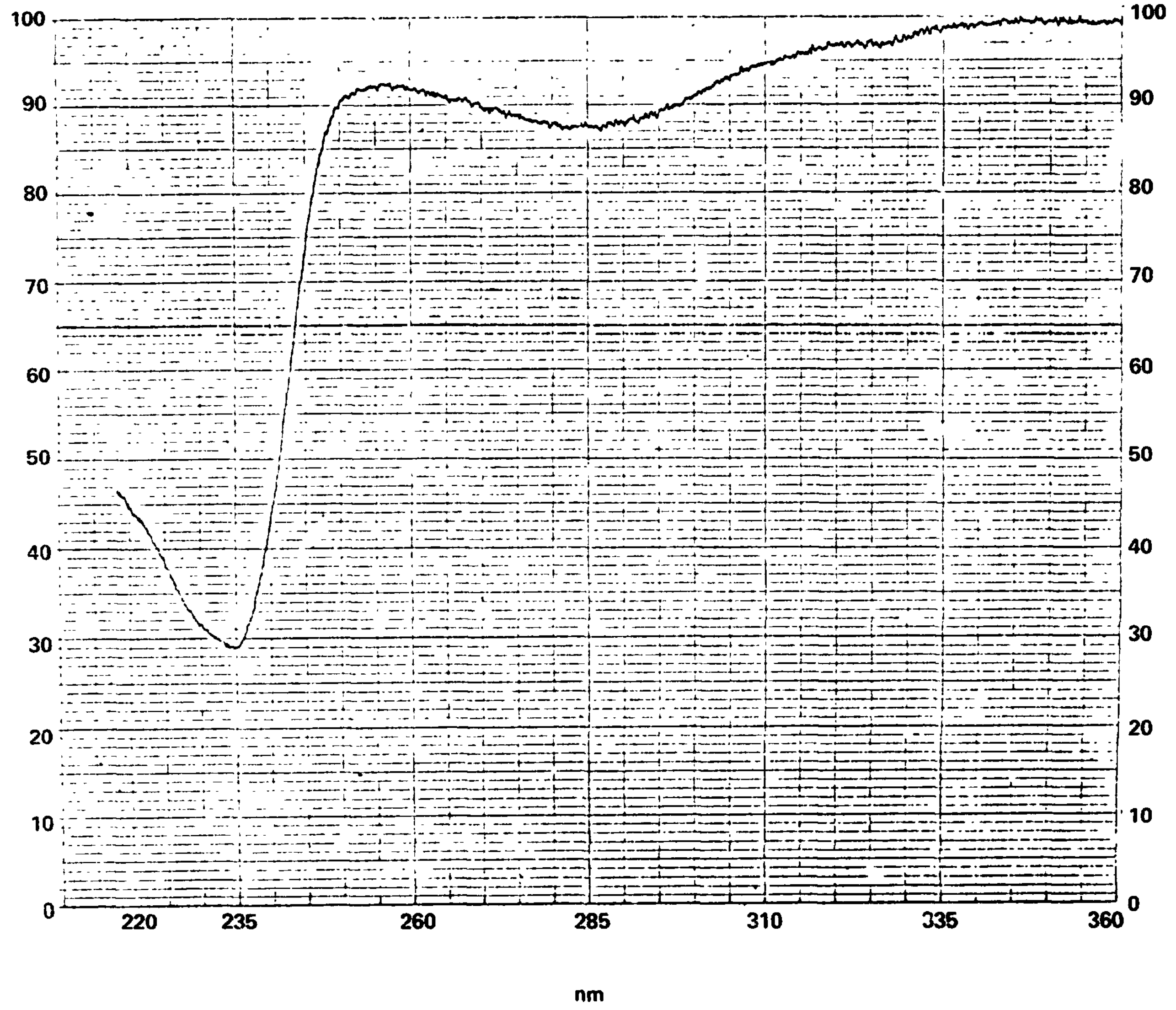

Figure 14. P-10 Oil, di (2 ethyl hexyl) sebacate
Equivalent Thickness 1.58×10^4 A

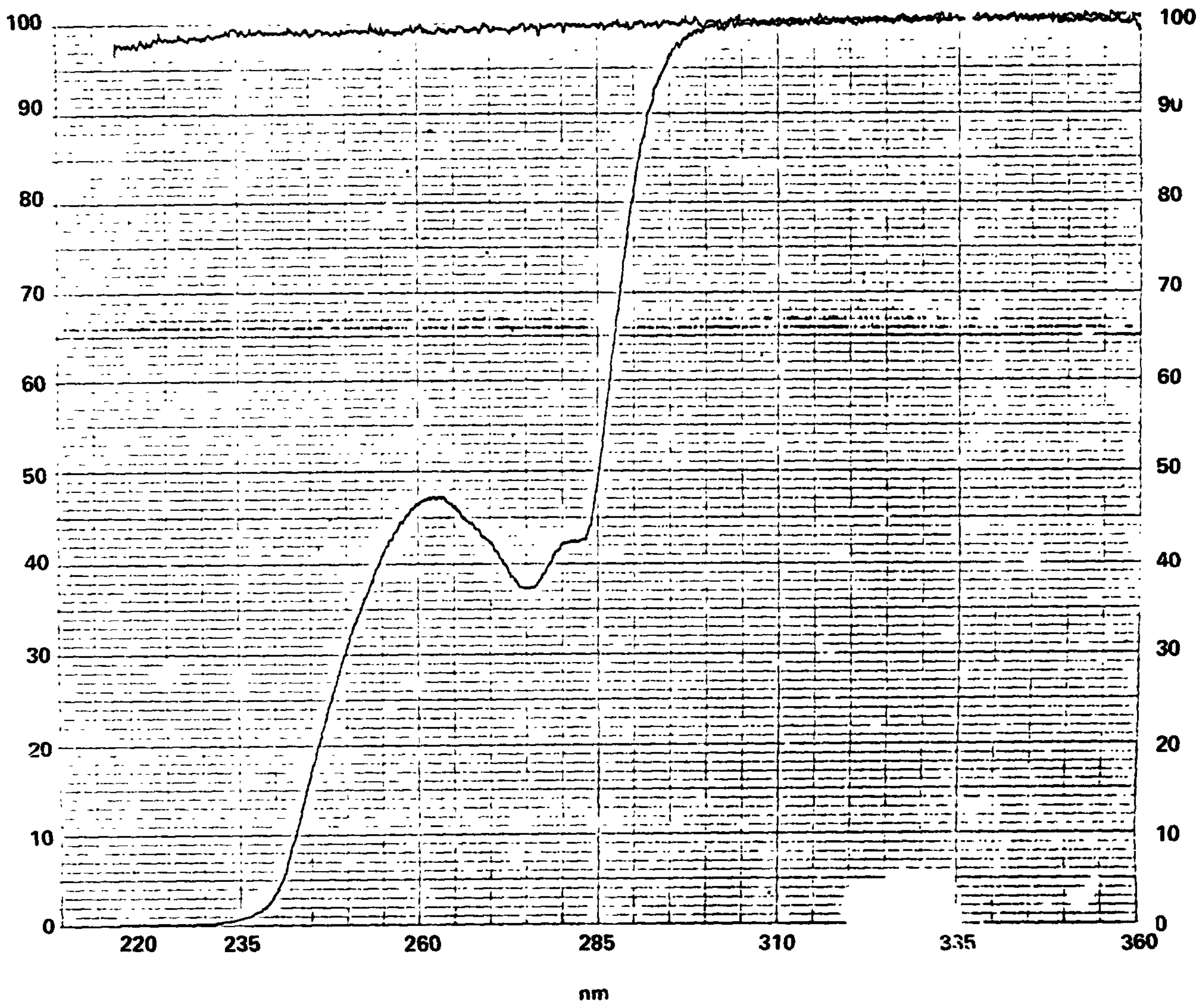

Figure 15. Di (2-ethyl hexyl) phthalate (DEHP) – plasticizer
Equivalent Thickness 1.58 × 10^4 A

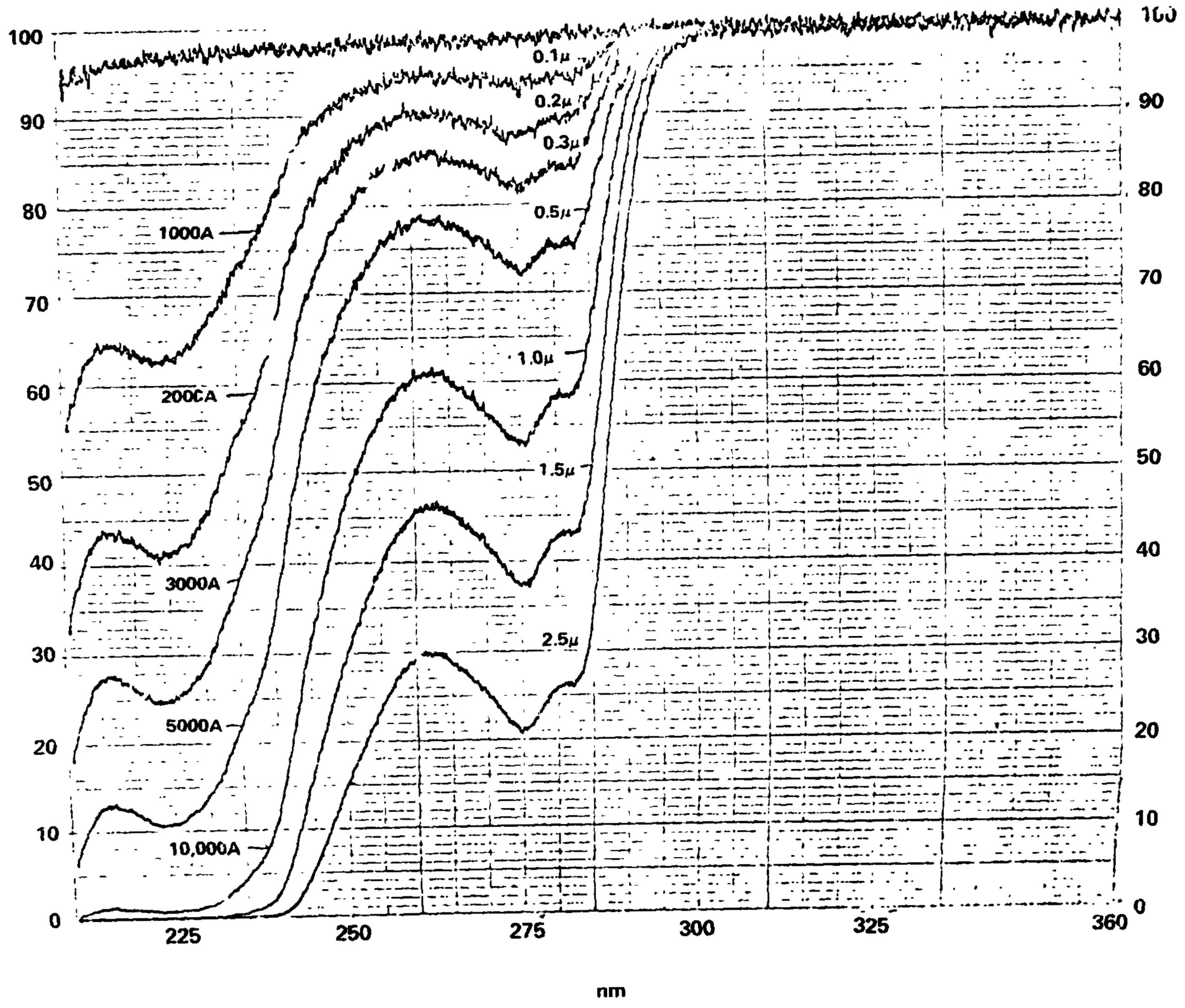

Figure 16. Di (2 ethyl hexyl) phthalate – 1000A-25,000A