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by the Research & Development Division of
Engelhard Industries, Inc., Newark, New Jersey;
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FOREWORD

This is the summary technical report describing work performed by the Research and Development Division of Engelhard Industries, Inc., under Contract No. AF 33(616)-7849 for the Air Force Materials Laboratory, United States Air Force. This contract was initiated under Project No. 7340, "Nonmetallic and Composite Materials," Task No. 734007, "Coatings for Energy Utilization, Control and Protective Functions." Mr. James H. Weaver of the Nonmetallic Materials Division served as project engineer.

This report covers work conducted from 1 February 1962 to 30 April 1963 under Part II of this contract. Work conducted previously has been published as ASD-TDR-62-92, Part I. In the interest of brevity, none of the material in the Part I report will be repeated here.

The investigation was conducted by Robert C. Langley, James S. Hill and Henry J. Albert, all of the Research and Development Division. Most of the samples were prepared by Edith Verlezza of the Hanovia Liquid Gold Division and her work is hereby acknowledged.

Reflectance measurements in the visible and near infra-red were made by a sub-contractor, Electrical Testing Laboratories, Inc., of New York City. The authors wish to acknowledge the assistance of Mr. Roger Keith of the University of Dayton Research Institute in obtaining reflectance measurements over the range of 1.5 to 15.0 microns.

ABSTRACT

In this research it was found that a film, about 1250 angstroms thick, of gold, rhodium and oxides of bismuth, barium, chromium and silicon could be reproducibly obtained on a variety of diffusion barriers on Inconel. This was done by a single brush or spray application of an organic solution, followed by thermal decomposition in the air.

Total reflectance measurements before and after samples were subjected to elevated temperatures in high vacuum indicate that on vacuum deposited cerium oxide the gold-plus-oxides film is essentially unchanged after 50 hours at 800°C in a vacuum of 0.3×10^{-5} torr. Under the same conditions of time and vacuum at 600°C, the film is unchanged over diffusion barriers obtained from National Bureau of Standards Frit A-418 and over films of cerium oxide about 1000 angstroms thick obtained by thermal decomposition of organic compounds.

Reflectance of the film at wavelengths below 1.5 microns can be decreased by overcoating with a film of aluminum oxide about 1000 angstroms thick obtained by thermal decomposition of an organic solution of aluminum.

Solar collector surfaces having good stability at elevated temperatures in a space environment can be easily produced by the methods used in this investigation.

This technical documentary report has been reviewed and is approved.



J. M. KELBLE, Chief
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I INTRODUCTION

In Part I of this research, a gold film containing rhodium and oxides of bismuth, barium, chromium and silicon was developed on glass. Specular reflection measurements indicated that this film absorbed energy of wavelengths shorter than 1.5 microns while reflecting as well as polished aluminum in the range of 1.5 to 15 microns. These optical properties make the film potentially useful in converting solar energy to heat in space since they indicate a combination of high solar absorptance together with low total hemispherical emittance. A detailed discussion may be found in the literature.^{1,2}

One goal of the current investigation was to apply the most promising trial (identified as Solution No. 94) developed in Part I by practical methods such as brushing or spraying in place of the spinning technique used in Part I, without loss of desirable optical properties.

Another goal was to apply the coating on a metallic substrate capable of continuous operation at elevated temperatures. Inconel was chosen and this meant that a diffusion barrier suited to this substrate must be used to prevent failure of Film No. 94. Macklin, Withers and Schatz³ had found that NBS Frit A-418, nickel oxide, cerium oxide and silicon monoxide were promising in preventing diffusion between Inconel and pure gold films at elevated temperatures and it was decided to emphasize these materials in an attempt to make a laminate of Film No. 94 - diffusion barrier - Inconel capable of operating, without change in optical properties, for 50 hours at 800°C in a vacuum of 5×10^{-5} torr. The temperature range originally specified in this task was 250 to 800°C but early in the investigation emphasis was changed toward the upper limit since diffusion problems are minor at low temperatures.

Glass was used as the substrate to determine a reproducible technique for applying Solution No. 94. Once a method had been chosen, it was used for the production of Inconel samples on which diffusion barriers had been applied by various techniques. Vacuum deposition was used for the application of silicon monoxide and cerium oxide. Flame spraying was used to apply aluminum oxide and was also tried, without success, with zirconium oxide. Frit A-418 was applied by the usual method of spraying from a water slurry while other frits were applied by the dry powder method. Nickel oxide was applied by electroplating nickel on Inconel and heating in air to form nickel oxide.

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Aluminum oxide, cerium oxide and nickel oxide were also applied by a novel method. Organic solutions of organic compounds of these metals were made and were sprayed on Inconel. Firing in air to 600°C gave very thin films of the oxides. This proved to be a practical application method and films of aluminum oxide and cerium oxide about 1000 Angstroms in thickness were effective diffusion barriers.

At a meeting with the project engineer in May 1962, a change to very thin diffusion barriers was agreed upon, so thermal decomposition of metallo-organic compounds assumed greater importance. This change made the surface finish of the Inconel much more critical than when substantial films (e.g., several mils) are used as diffusion barriers. A considerable part of the effort was given over to investigating Inconel finishing techniques suited to our goals.

As samples of Film No. 94 - diffusion barrier - Inconel were made, reflection of Film No. 94 was measured. All measurements made in Part I of this work were of specular reflection. Since the substrate was glass, the gold film was a mirror and these measurements were valid. Early in this investigation, it was found that on most diffusion barriers the thin gold film had a substantial element of non-specular reflection so a change to total reflectance measurements was made. All measurements over the range of 430 to 1100 millimicrons given in this report are of total reflectance in terms of magnesium oxide having a reflectance of 0.98.

After measurement the samples were heated for 50 hours at varying temperatures in a vacuum of 0.3×10^{-5} torr and reflectance was again measured. Those samples showing no significant change in reflectance were considered stable at the test temperatures.

Toward the conclusion of the investigation, a few trials were made toward increasing the thermal stability and the solar absorption of Film No. 94 by overcoating it with a transparent film of aluminum oxide. Schatz and McCandless⁴ have reported success with vacuum evaporated films of aluminum oxide and other dielectrics over pure gold films. Our approach was the spray application of an organic solution of aluminum followed by thermal decomposition to form aluminum oxide. Results were encouraging and it appears that reflectance of Film No. 94 below 1.5 microns can be decreased significantly in this way without great decrease in reflectance in the 1.5 to 15.0 microns range. This may have particular importance since Film No. 94 was developed solely by empirical methods while quarter wavelength layers to obtain selective anti-reflection can be calculated from firmly established theory. Papers by Cox, Hass and Rowntree⁵ and Young⁶ are typical of the large literature on this subject.

II EXPERIMENTAL

Brush and Spray Application of Solution No. 94

At the start of this investigation it was considered that optical results reproducing those obtainable by the spinning technique with Solution No. 94 should be possible with brush or spray application. To achieve this, it was thought that a mechanically controlled spray gun might be used or that a color standard might be established for controlling thickness of wet application.

To determine reproducibility of samples made by spraying, a soluble red dye was added to Solution No. 94 and the dyed solution was sprayed heavy, medium and light on flat soda-lime glass. The operator attempted to make each class uniform by judging the color of the wet application. In this way all samples in the "light" group appeared of uniform color and less intense in color than those called "medium". Twelve samples were done in each group; two samples were retained unfired as possible standards and the remaining ten in each group were fired to 600°C in air through a continuouslehr on a standard cycle of 1.5 hours.

After firing, an attempt was made to distinguish between the light, medium and heavy groups by measuring electrical resistance with a portable ohmmeter. All were so conductive that no ready distinction was possible with the instrument used. Three samples were chosen at random from each group and total reflectance of these nine samples was measured over the visible range using a G. E. recording spectrophotometer and a magnesium oxide standard. Excellent reproducibility was found among the three samples in each group and good reproducibility was found among groups. Figure 1 gives curves for the three samples of the "medium" group measured and Figure 2 gives curves chosen at random from all three groups.

Another group of 36 samples was made using dyed Solution No. 94 applied to flat glass by brushing "light", "medium" and "heavy" applications. After firing in air on the standard cycle, four random samples from each group were measured for total reflectance over the visible range. Excellent reproducibility was found within each group and there was good reproducibility among the three groups. Figure 3 gives curves for the four samples measured from the "medium" group.

Production of over 200 further samples by brushing Solution No. 94 in "medium" application over a wide variety of diffusion barriers gave no difficulty in obtaining reproducible optical results. It was found that the addition of red dye was not necessary for a moderately skilled technician to obtain reproducibility of wet application.

Surface Finish of Inconel

Thin (50 mils) Inconel, two inches square, was used for almost all of the sample preparation. In early work, when substantial flame sprayed coatings of aluminum oxide were used, thin Inconel tended to warp so 0.25 inch thicknesses were used. Before emphasis shifted to very thin diffusion barriers, the Inconel was cleaned by degreasing with successive washes of carbon tetrachloride and benzene and sandblasting was then the only surface treatment before flame spraying or application of frit.

Since some of the diffusion barriers would have thicknesses of less than 1000 Angstroms, various means were tried to obtain a surface finish on Inconel close to that found on glass, i.e., about 0.5 microinch. Single grinding with a silicon carbide wheel gave a finish of 30-45 microinches. These measurements were made on a Micrometric Profilometer. Double grinding with a fine grained alumina wheel used after the silicon carbide wheel gave a surface finish of 5-11 microinches. Electropolishing of doubly ground samples produced a surface of 3 microinches but due apparently to preferential etching, the surface was left with pits, furrows and spongy areas and was not suitable for use with thin diffusion barriers.

A finish of 4 microinches was obtained when doubly ground samples were buffed. This technique was expensive, and apparently a tenacious film of rouge remained on the Inconel and this gave difficulty in subsequent coating.

Rolled samples were honed and this gave a surface finish of 2-4 microinches which took coatings well. To allow a choice to be made between honing and double grinding, Inconel prepared by both methods was coated with nickel oxide, aluminum oxide and cerium oxide diffusion barriers. These films were about 1000 Angstroms thick. Gold film No. 94 was developed over these diffusion barriers in a film about 1250 Angstroms thick. Total reflectance of the samples was then measured over the visible range. There was no significant difference between the samples in the three groups. Figures 4 and 5 show that reflectance curves of Film No. 94 over aluminum oxide on both honed and doubly ground Inconel are identical.

Diffusion Barriers - Frits

Pfaudler Frit No. 53 was ground to a particle size of less than 10 microns and applied to Inconel by spraying a single coat from an alcohol-water suspension and firing at 880°C. This frit was also applied to Inconel by sifting three coats of the frit

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on to dry Inconel and firing each coat at 880°C. Spray application gave a frit thickness of .002" while the dry powder method gave a thickness of .015". Solution No. 94 was brushed on these samples and developed on the standard firing cycle of 600°C. To determine reaction of the frit as the melting point was approached, Solution No. 94 was also developed over it at 700°C and at 800°C. The gold film developed at 600°C was of normal appearance and almost specular on this glossy frit. At 700°C an incipient crazing of the gold was noted and at 800°C a definite crazing of the gold coating appeared. Figure 6 gives total reflectance of Film No. 94 developed at 600°C over Frit No. 53 having a thickness of .015".

Several specimens were coated with Pemco Frit No. P 279 by the dry powder method and fired at 600°C. A sample was also made with P 279, to which 5% of chromic oxide had been added. Frit thickness in all cases was held to about .005". Film No. 94 was developed on these samples at the usual firing temperature of 600°C before this approach was discontinued because of the low melting point of this frit.

Pemco Frit No. 230 was tried because it has a melting point of 1050°C but adherence was obtained only in localized areas on sandblasted Inconel.

National Bureau of Standards Frit A-418 was prepared as described in ASD-TR-61-5 except that grinding time was increased to 120 hours to produce a powder finer than 5 microns. This was suspended in water, sprayed on sandblasted Inconel and fired at 1010°C for three minutes. Film thickness was .001". Solution No. 94 was brushed on several samples made in this way but after firing it was found that there was electrical resistance of only 10 ohms between gold film and Inconel.

Throughout this investigation, Solution No. 94 was brushed over all diffusion barriers with care taken to avoid contact with exposed Inconel at the edges. Low electrical resistance between the fired gold film and Inconel was taken as an indication that the diffusion barrier was either too thin generally or that it contained voids.

About 20 samples were given two coats of A-418 and two firings at 1010°C and it was found that frit thickness could be held close to .002". When Film No. 94 was developed over these samples, electrical resistance between gold and Inconel was usually 1,000,000 ohms or higher. We took this as an indication that Frit A-418 would not be an effective diffusion barrier when used in less than this thickness.

Fifteen samples of Film No. 94 - A-418 - Inconel were measured for total reflectance over the range of 430 to 1100

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millimicrons. In all cases the frit was .002" thick. Reproducibility was very good. Three samples were measured for total reflectance over the range of 1.5 to 15.0 microns. Reproducibility was excellent and the samples had slightly better reflectance than the standard, an electropolished aluminum mirror. These data are given later.

Diffusion Barriers - Flame Sprayed

Because warping of thin Inconel presented a problem, all samples made by the flame spray technique had 0.25 inch Inconel as substrate. Aluminum oxide from alumina spray rod and from powder having a density greater than 98% of theoretical, was applied from an oxyacetylene torch. Twenty-two samples were made with alumina thickness ranging from .005" to .040". The alumina appeared to adhere well and no scaling was observed after heating to 600°C in air. The surface roughness of the alumina ranged from 600 to 800 microinches, and grinding was necessary because of the very thin film (about 1250 Angstroms) obtained from Solution No. 94. A diamond impregnated wheel was used in the grinding operation and best results were obtained when an initial alumina thickness of .020" was ground to .010". Surface roughness then varied from 30 to 80 microinches.

Most of the alumina samples made by flame spraying were very porous and Solution No. 94 was absorbed immediately upon application. After firing on the standard 600°C cycle, a purple stain, rather than a gold film resulted. This stain was not electrically conductive and confirmed the impression that the wet application had been absorbed. A second coat of Solution No. 94 was applied to one of the samples. After firing there was some improvement but the film was conductive only in one small area. An attempt was made to seal the surface pores of several samples by coating with a concentrated solution of aluminum nitrate and firing to 1000°C in air. When Solution No. 94 was brushed on these samples it was absorbed to a lesser extent than on alumina samples not treated with aluminum nitrate, but the fired films obtained were still purple and non-conductive.

On one flame sprayed alumina sample, Solution No. 94 gave a gold film of uniform appearance after a single brushed application was fired to 600°C. This film was conductive and when measured for reflectance over the range of 430 to 1100 millimicrons gave a curve similar to that of Film No. 94 on other diffusion barriers. No reason for the apparent low porosity of this alumina film was found before the flame spray approach was dropped because of the thickness of the diffusion barriers obtained by this technique.

Several attempts to flame spray zirconium oxide were not successful as poor adherence could not be overcome.

Diffusion Barriers - Electroplated

Previous workers (Ref. 3) had found nickel oxide a promising diffusion barrier between pure gold and Inconel. Eight pieces of Inconel were chemically cleaned and electroplated with nickel to a thickness of .0001". The nickel film was then converted to nickel oxide by heating in air at 800°C for 48 hours. None of the samples had any surface conductivity. Film No. 94 was developed over the nickel oxide in the usual way and reflectance measurements over the 430-1100 millimicron range gave the usual curve. It was found that electrical resistance between gold film and Inconel was low, about 6-10 ohms, on this group of samples.

Because gold does not alloy to any significant extent with rhodium, it was thought that a thin rhodium electroplate on Inconel might prevent diffusion between Film No. 94 and Inconel. A flash coating of rhodium was electroplated on honed Inconel. Film No. 94 was developed over the rhodium by firing on the standard cycle, and had the usual reflectance values over 430 to 1100 millimicrons.

Diffusion Barriers - Vacuum Deposited

Five honed Inconel samples were coated with cerium oxide by the vacuum technique described in Reference 3. This was done by the Research and Development Division of American Machine and Foundry Company under the supervision of Dr. E. A. Schatz. The cerium oxide coatings varied from 0.6 to 9.1 mg/cm². The surface of the thinnest sample and of a sample having 3.4 mg/cm² was semi-bright while samples having thicker coatings were matte. As Solution No. 94 was brushed on these samples, there was some indication of absorption by the cerium oxide, indicating a porous structure. After firing at 600°C, Film No. 94 was conductive on all five samples and there was very little electrical resistance between gold and Inconel. Reflectance values showed good reproducibility and the thinnest and thickest cerium oxide samples gave almost identical curves.

Eight doubly ground Inconel samples were coated with silicon monoxide by the vacuum technique. Film thickness was held between 1.0 and 1.5 mg/cm², a range which proved useful to previous workers (Ref. 3). After development of Film No. 94, it was noted that electrical resistance between gold and Inconel was only 30 to 40 ohms. Three of these samples had a curious type of failure; after firing of the gold film on the usual cycle, the samples appeared normal but within 4 to 5 days both diffusion barrier and gold films had flaked off simply on standing at room temperature. This flaking covered from 75 to 95% of the surface of each sample. The Inconel exposed was perfectly bright and had no evidence of surface oxidation. The small size of the flakes and their shape did not suggest spalling due to differences in expansion, and this is not usually a problem when very thin films are involved.

Three of the silicon monoxide samples were measured for total reflectance and the usual curve of Film No. 94 was obtained with good reproducibility among the samples.

Diffusion Barriers - Thermal Decomposition of Metallo-Organics

In Part I of this research, about 40 metals were made organic soluble by putting them in the form of metallo-organic compounds. This was done to allow addition of them in minor amounts to an organic gold solution. These organic compounds of base metals are usually carboxylates or alcoholates but they are commonly called "resinates". Details of their manufacture may be found in Ballard⁷ or Morgan and Wagner⁸.

In this investigation, the use of very thin oxide films obtained by the thermal decomposition of metallic resins seemed a good approach to diffusion prevention and organic solutions of aluminum, nickel and cerium were made. These were formulated to have flow, viscosity and drying properties suitable for spray application. Table 1 gives these formulations.

The solutions were sprayed on doubly ground Inconel until the application flowed together just enough to form a wet, glossy film. The coatings were then fired in air on the same cycle used for Solution No. 94. The thickness of the film obtained in a single application was estimated as follows. One hundred grams of any of the three solutions in Table 1 covers 66 square feet. In the case of the solution containing 2.0% cerium, calculated as CeO_2 , the film thickness is about 450 Angstroms, assuming that the cerium oxide is of theoretical density (7.3). This assumption is questionable, and the situation becomes more complex when it is considered that the oxide film adhered well to the Inconel and probably had undergone chemical reaction with the substrate. Since all of the samples having very thin diffusion barriers were made with 2, 4 or 6 coats, film thickness is expressed as "about 1000 Angstroms" or "about 2000 Angstroms". Expressed as weight per unit area, a single application of the cerium solution gave a fired film, by calculation, of $.00003 \text{ g/cm}^2$. Six coats gave a film considerably thinner than the vacuum deposited cerium oxide samples described above.

About 90 samples of doubly ground Inconel were prepared with 2, 4 or 6 coats of aluminum oxide, cerium oxide and nickel oxide by the thermal decomposition technique. In all cases the oxide films were bright, iridescent, adherent films of glossy appearance. Samples made with 4 and 6 coats seemed to be insulators when tested with an ohmmeter but after Film No. 94 had been developed over all 90 samples, electrical resistance between gold and Inconel was only about 30 ohms. Reproducibility of reflectance of Film No. 94 was good. Figures 4 and 5 show identical curves obtained with Film No. 94 over two coats of aluminum oxide.

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TABLE 1

Cerium Solution for Spraying (2.0% CeO₂)

	<u>grams</u>
Cerium resinate dissolved in a mixture of oil of rosemary, nitrobenzene and toluene (5% CeO ₂)	36.0
Rosin dissolved in oil of spike (50% rosin)	27.0
Oil of lavender	9.0
Oil of camphor	9.0
Oil of petitgrain	9.0
	<u>90.0</u>

Aluminum Solution for Spraying (1.67% Al₂O₃)

Aluminum resinate dissolved in a mixture of oil of rosemary, nitrobenzene and toluene (5% Al ₂ O ₃)	33.3
Rosin dissolved in oil of spike (50% rosin)	33.3
Oil of lavender	11.1
Oil of camphor	11.1
Oil of petitgrain	11.2
	<u>100.0</u>

Nickel Solution for Spraying (4.0% NiO)

Nickel resinate dissolved in a mixture of oil of rosemary, nitrobenzene and toluene (6% NiO)	60.0
Rosin dissolved in oil of spike (50% rosin)	15.0
Oil of lavender	5.0
Oil of camphor	5.0
Oil of petitgrain	5.0
	<u>90.0</u>

High Temperature - High Vacuum Tests

As Film No. 94 - diffusion barrier - Inconel samples were prepared, reflectance of Film No. 94 was measured over the range of 430 to 1100 millimicrons. Groups of samples having various diffusion barriers were then subjected to high temperatures plus high vacuum and remeasured to determine stability of the laminates. In all cases the vacuum used was 0.3×10^{-5} torr and the time at temperature was 50 hours.

The samples were heated in a vacuum annealing furnace designed and built at the Engelhard Industries, Inc. Research and Development Division. This is a cylindrical furnace having a steel shell lined with 7-1/2 inches of refractory brick at the center of which lies a fused quartz tube. This tube has a five inch bore by 48 inches long capable of withstanding a vacuum of 0.35×10^{-5} torr at a maximum temperature of 1000°C. It is an electrically heated furnace in which six equally spaced silicon carbide heating elements run lengthwise around a nine inch diameter circle thereby giving a uniform hot zone of 24 inches. Samples are fed into the hot zone in a molybdenum boat approximately 36 inches long and 4 inches wide. In tandem with the furnace proper is a cooling chamber which permits evacuation of the complete system prior to feeding samples into the hot zone. This is accomplished by a chain drive attached to the boat which is manually operated. Thus, samples enter into the cold zone, are evacuated, charged into the hot zone, withdrawn into the cold zone - still in vacuum - and finally released to the atmosphere at room temperature.

Cycles were run at temperatures of 250, 500, 600, 700 and 800°C. As anticipated, there was no change after the 250°C cycle and a control with Film No. 94 applied directly on doubly ground Inconel had not changed either.

Vacuum Cycle at 500°C

After the vacuum cycle at 500°C, a control sample of Film No. 94 on fused quartz had not changed but a control sample of Film No. 94 directly on doubly ground Inconel had changed; the gold film had disappeared. Samples made with Frit A-418, Pfaudler Frit No. 53, vacuum deposited cerium oxide (9.1 mg/cm^2), cerium oxide from organic solution (2 coats, about 1000 Angstroms) and aluminum oxide from organic solution (2 coats, about 1000 Angstroms) had no apparent change. Reflectance measurements confirmed that these samples had not changed. A sample made with 2 coats of nickel oxide had changed; the iridescent appearance of the diffusion barrier had disappeared and the gold film had become weak in color. Figure 7 shows reflectance of this sample before and after the vacuum cycle at 500°C. Film No. 94 over rhodium electroplated on Inconel had changed in appearance and in reflectance values in a manner very similar to the nickel oxide sample.

Vacuum Cycle at 600°C

After the vacuum cycle at 600°C, samples made with 2, 4 and 6 coats of cerium oxide from organic solution and with 2, 4 and 6 coats of aluminum oxide from organic solution showed no apparent change. Reflectance measurements confirmed that Film No. 94 on the three cerium oxide samples had not changed. Figures 8, 9 and 10 give reflectance curves before and after this cycle for these three samples. Reflectance measurements of the aluminum oxide samples indicated that reflectance of Film No. 94 had increased about 5% on the two samples with thinner diffusion barriers, but that the increased reflectance was about 20% on the sample with 6 coats of aluminum oxide. Figures 11, 12 and 13 compare these samples before and after this cycle. Film No. 94 on a quartz control had not changed. A sample made with vacuum deposited cerium oxide (3.4 mg/cm²) had no apparent change. A sample made with Frit A-418 also appeared unchanged. Figure 14 gives reflectance of this sample before and after vacuum cycle at 600°C. A sample made with Pfaudler Frit No. 53 .002" thick had changed in that the frit had bubbled and blistered but the gold film appeared unchanged. Figure 15 indicates that Film No. 94 on this frit has undergone only slight change in reflectance. Nickel oxide samples made by the electroplating technique and by depositing 2, 4 and 6 coats from organic solution had changed with the nickel oxide films losing iridescence and the gold films losing their yellow color to a considerable extent. Figure 16 shows the change caused by this cycle in an electroplated sample (.0001" nickel). Figure 17 shows the change in a sample made with 6 coats of an organic nickel solution.

Vacuum Cycle at 700°C

After the vacuum cycle at 700°C, Film No. 94 on a quartz control had become matte, transparent, non-adherent and had lost electrical conductivity. Nickel oxide samples made by the electroplating technique and from organic solution had failed in the same manner observed after cycles at lower temperatures. Pfaudler Frit No. 53 .002" thick was badly blistered and Film No. 94 on it had changed to a non-conductive uniform light tan film. Figure 18 shows the marked decrease in reflectance of this sample. Frit A-418 had become matte and Film No. 94 on it had become uniformly matte and brown in color and was non-conductive. Figure 19 gives reflectance of this sample. A sample made with cerium oxide vacuum deposited to a weight of 5.2 mg/cm² had changed very little. Figure 20 gives reflectance before and after the 700°C cycle for this sample. Film No. 94 on diffusion barriers made with 2, 4 and 6 coats of cerium oxide from organic solution showed change, but less with the thicker coats. Figure 21 compares these three samples. Film No. 94 on 2, 4 and 6 coats of aluminum oxide from organic solution had changed in that reflectance had increased.

Figure 22 shows the change after the cycle at 700°C for the sample made with 6 coats of aluminum oxide.

Vacuum Cycle at 800°C

Two vacuum cycles were run at 800°C, and the results confirmed those of cycles at lower temperatures. Film No. 94 on a quartz control had the same type of change observed after the 700°C cycle. Frit A-418 changed as noted above. All nickel oxide samples failed. Samples made with 2, 4 and 6 coats of cerium oxide from organic solution had greatly decreased reflectance. Samples made with 2, 4 and 6 coats of aluminum oxide from organic solution had changes in reflectance which differed according to the thickness of the aluminum oxide film. Figure 23 compares reflectance after the 800°C cycle of Film No. 94 on diffusion barriers formed from 2, 4 and 6 coats of aluminum oxide.

A sample made with cerium oxide vacuum deposited to a weight of 5.4 mg/cm² had a noticeable change in the appearance of Film No. 94 after the 800°C cycle, but a second sample made with a vacuum deposited weight of 3.4 mg/cm² sample had very little change. Film No. 94 on the 5.4 mg/cm² sample had disappeared from 2/3 of the surface and the remaining gold was not electrically conductive and had poor abrasion resistance. Film No. 94 on the 3.4 mg/cm² had no apparent change in appearance, conductivity or adherence. This sample was the most promising of the entire investigation, particularly since it had also been cycled for 50 hours at 600°C before the 800°C cycle. Figure 24 gives reflectance curves of Film No. 94 on vacuum deposited cerium oxide (3.4 mg/cm²) before and after the 600°C cycle and after the 800°C cycle.

Because of difficulties in preparing samples, silicon monoxide diffusion barriers applied by vacuum deposition were tested only on the 800°C cycle and on the 250°C cycle. As noted above, the 250°C test was too mild to permit proper evaluation of diffusion barriers. After the 800°C cycle, the silicon monoxide samples had the same type defect observed earlier. The silicon monoxide had flaked away from the Inconel over 50% or more of the surface area. This defect is distinct from failure of samples by diffusion.

Overcoating Film No. 94

A few samples were made to determine whether the change of Film No. 94 on most samples in the 800°C cycle was due to volatilization of one or more of the components of the film rather than to failure of diffusion barriers. Two coats of aluminum oxide (about 1000 Angstroms) were developed from organic solution over Film No. 94 on samples having as diffusion barriers silicon monoxide, 6 coats of cerium oxide from organic solution, 4 coats of aluminum oxide from organic solution and 6 coats of aluminum oxide from organic solution. After firing in air on the standard

cycle, the aluminum oxide films were transparent, iridescent and of glassy appearance. Some interesting reflectance results were found with these samples; these will be discussed below. After an 800°C vacuum cycle, reflectance measurements disclosed that overcoating Film No. 94 with aluminum oxide had not improved stability of these 4 samples.

Figure 25 is the reflectance of Film No. 94 over aluminum oxide developed from 4 coats of organic solution (about 2000 Angstroms). Figure 26 is a sample made in the same way but with 2 coats of aluminum oxide (about 1000 Angstroms) applied over Film No. 94. The decrease in reflectance due to the overcoating is interesting. Total reflectance of these samples was also measured over the range of 1.5 to 15.0 microns and the overcoated sample duplicated the uncoated sample except that the overcoating caused a decrease in reflectance of less than 10% between the range of 2.5 to 4.0 microns. Peak decrease was at 2.8 microns. Reflectance measurements of other overcoated samples in the 430 to 1100 milli-micron range and in the 1.5 to 15.0 micron range were similar.

Total Reflectance in the Range 1.5 to 15.0 Microns

Fifteen samples were measured for total reflectance in terms of an electropolished aluminum standard over the range of 1.5 to 15.0 microns. All samples tested gave curves quite close to that of the standard over the entire range. The best result was obtained with Frit A-418 as the diffusion barrier. Three samples were measured from 1.5 to 15.0 microns and the curves were essentially identical and slightly better than the standard. Figure 27 gives the comparison of one sample of Film No. 94 - A-418 - Inconel versus the standard.

Durability of Test Samples

Film No. 94 on all samples adhered well to the diffusion barrier after firing in air. The flaking experienced with silicon monoxide samples resulted in loss of adherence at the silicon monoxide-Inconel interface, not at the interface of Film No. 94-silicon monoxide. On more promising diffusion barriers such as Frit A-418 and cerium oxide, adherence of Film No. 94 was superior to that described in Part I of this film on glass. A standard firing cycle with a peak temperature of 600°C was used to prepare all samples in this investigation. Considerable improvement in durability on the better diffusion barriers may be obtained by firing in the range of 750-900°C in preparing the samples. A few trials at varying temperatures for varying times would lead to an optimum cycle for durability of Film No. 94 on a particular diffusion barrier, but time did not allow these experiments to be made.

III DISCUSSION

The preparation of 36 samples by spraying Solution No. 94 and of approximately 250 samples by brushing a "medium" application of Solution No. 94 demonstrated that the optical properties obtained with the spinning method could be duplicated by more practical application techniques. About 150 samples were measured, before vacuum tests, over the range of 430 to 1100 millimicrons. Total reflectance values of Film No. 94 on all these samples were reproduced within a range of approximately $\pm 10\%$. On specific diffusion barriers reproducibility was better than this figure and in many cases substantially duplicate curves were obtained. Similarly, reproducibility was good among samples measured over the 1.5 to 15.0 micron range and these total reflectance values were in good agreement with specular reflection values of Film No. 94 on glass reported in Part I.

No serious problem now remains to the use of Film No. 94 on Inconel provided the Inconel is first coated with a diffusion barrier suited to maximum operational temperature. To produce such laminates, Solution No. 94 can be brushed on the diffusion barrier without elaborate control of application. Firing in air on the cycle used throughout this investigation or on a cycle better suited to the particular diffusion barrier can be accomplished in standard laboratory or production furnaces.

The behavior in this investigation of some diffusion barriers found by previous workers (Ref. 3) as useful on Inconel requires an explanation. In the case of nickel oxide, failure to prevent diffusion between Film No. 94 and Inconel took place in the vacuum cycle at 500°C, and was confirmed in 4 cycles at higher temperatures. Even at 500°C, the gold films had apparently disappeared and this was true of nickel oxide samples made both by electroplating nickel and by deposition of varying thicknesses of nickel oxide from organic solution. Yet Film No. 94 was developed on these samples by firing at 600°C in air on a cycle with the samples above 500°C for approximately 35 minutes. A possible explanation is that when heated in a vacuum, nickel oxide is reduced to nickel which then diffuses both into the gold film and into the Inconel. Time did not permit an experiment in proof but on all nickel oxide samples which had failed it was observed that the diffusion barrier had undergone obvious change in appearance even at the edges which were not coated with Film No. 94. Our results do not necessarily contradict those of previous workers whose tests of nickel oxide on Inconel were run in air.

The poor results obtained with Film No. 94 applied over vacuum deposited silicon monoxide are not attributed to diffusion between gold and Inconel. Some samples failed at room temperature, 4 to 5 days after firing in air at 600°C. On these samples and on others which had the same defect, flaking, after vacuum cycling

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at 800°C, the diffusion barrier appeared unchanged at the edges where it had not been coated with Film No. 94. This suggests that the oxides in Film No. 94 reacted with the silicon monoxide with the result that the bond between silicon monoxide and Inconel was weakened. Previous workers made their laminates by vacuum deposition of pure gold over silicon monoxide. Since Film No. 94 contains 10.1% by weight of metallic oxides, there is a possibility of such a reaction with silicon monoxide. Another fact suggesting reaction between oxides is the change in Film No. 94 on fused quartz when cycled in vacuum at 700°C and at 800°C. On these samples Film No. 94 became matte, transparent, non-adherent and lost electrical conductivity, but in the same cycles Film No. 94 on some cerium oxide samples was essentially unchanged.

Results obtained with National Bureau of Standards Frit A-418 indicate that this is a useful diffusion barrier when applied .002" thick on Inconel but that laminates made with this frit can not operate at 700°C for extended periods of time. The change in gloss of this frit after extended time at elevated temperatures has been reported by other workers and had previously been observed by us in other work when samples were heated in air at 760°C for 4 hours or longer.

Vacuum deposited cerium oxide diffusion barriers gave very promising results with Film No. 94. As shown in Figure 24, a sample made with 3.4 mg/cm² cerium oxide was essentially unchanged after the 800°C cycle and this sample had been exposed for a total time of 100 hours at 600°C and at 800°C. The change in a sample having a thicker deposit of cerium oxide after the 800°C cycle suggests that an optimum thickness limit exists with this material, but this could not be investigated within the time limits of this contract.

The stability after the 600°C vacuum cycle with samples having diffusion barriers of cerium oxide and with the thinner coats of aluminum oxide applied by the novel technique of thermal decomposition of organic compounds indicates that this method is a practical one for the production of laminates to operate at temperatures up to 600°C. Diffusion barriers made by this technique have all of the flexible application advantages of Solution No. 94. The application method has no limitation of size or complexity of shape of the substrate, no elaborate application equipment is needed and personnel do not need lengthy training to obtain reproducible results.

Another interesting point about diffusion barriers applied from organic solution is their effectiveness in extremely thin films, on the order of 1000 or 2000 Angstroms. Calculated on a weight per unit area basis, six applications of the organic solution of cerium give a fired film which is only about 5% of the

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3.4 mg/cm² of cerium oxide found promising by the vacuum technique. Unfortunately time did not permit sufficient experimentation to determine an optimum thickness for these very thin diffusion barriers. As shown in Figure 21, reflectance change of Film No. 94 over cerium oxide after the 700°C cycle was less over the thicker coats.

One of the reasons for making a few samples with Film No. 94 overcoated with about 1000 Angstroms of aluminum oxide was that volatilization from Film No. 94 was suspected as a cause of change in reflectance after vacuum cycling at 800°C. That volatilization is not a problem under these conditions was later demonstrated when a sample withstood this cycle with no substantial change in reflectance (Figure 24). Samples which were overcoated changed after cycling at 800°C so on these particular diffusion barriers (silicon monoxide and 2000 Angstrom films of cerium oxide and of aluminum oxide) changes in reflectance must be attributed either to reaction of Film No. 94 with the diffusion barrier or failure of the barrier to prevent diffusion between gold and Inconel.

Investigation of the effect on reflectance of Film No. 94 by the use of a transparent overcoat gave results which show the way to substantial improvement of the ratio of solar absorptance to total hemispherical emittance. As shown in Figures 25 and 26, the particular thickness of aluminum oxide used gave an appreciable decrease in reflectance at wavelengths of high solar radiation. This change, together with the small change in reflectance noted at 2.8 microns, strongly suggests that the improvement is due to optical interference. Taking advantage of the firm theory which has been developed on this subject, it should be a relatively simple matter to lower the reflectance shown in Figure 26. Dielectrics other than aluminum oxide could be applied over Film No. 94 by the same practical technique from organic solution.

IV CONCLUSIONS

A film, about 1250 Angstroms thick, of gold, rhodium and oxides of bismuth, barium, chromium and silicon has low total reflectance below 1.5 microns and high total reflectance in the range of 1.5 to 15.0 microns. Total reflectance measurements indicate that this film has high solar absorptance together with low total hemispherical emittance. The film can be readily obtained on a variety of substrates by a single brush or spray application of an organic solution, followed by thermal decomposition in air.

The film has good stability on Inconel at elevated temperatures in high vacuum provided a diffusion barrier separates the film from the substrate. Vacuum deposited cerium oxide is a diffusion barrier over which the gold-plus-oxides film remains unchanged after 50 hours at 800°C in a vacuum of 0.3×10^{-5} torr.

After 50 hours in vacuum at 600°C, the film is unchanged over diffusion barriers obtained from National Bureau of Standards Frit A-418 and over films of cerium oxide about 1000 Angstroms thick obtained by thermal decomposition of organic compounds.

Reflectance of the film at wavelengths below 1.5 microns can be decreased by overcoating with a film of aluminum oxide about 1000 Angstroms thick obtained by thermal decomposition of an organic solution of aluminum.

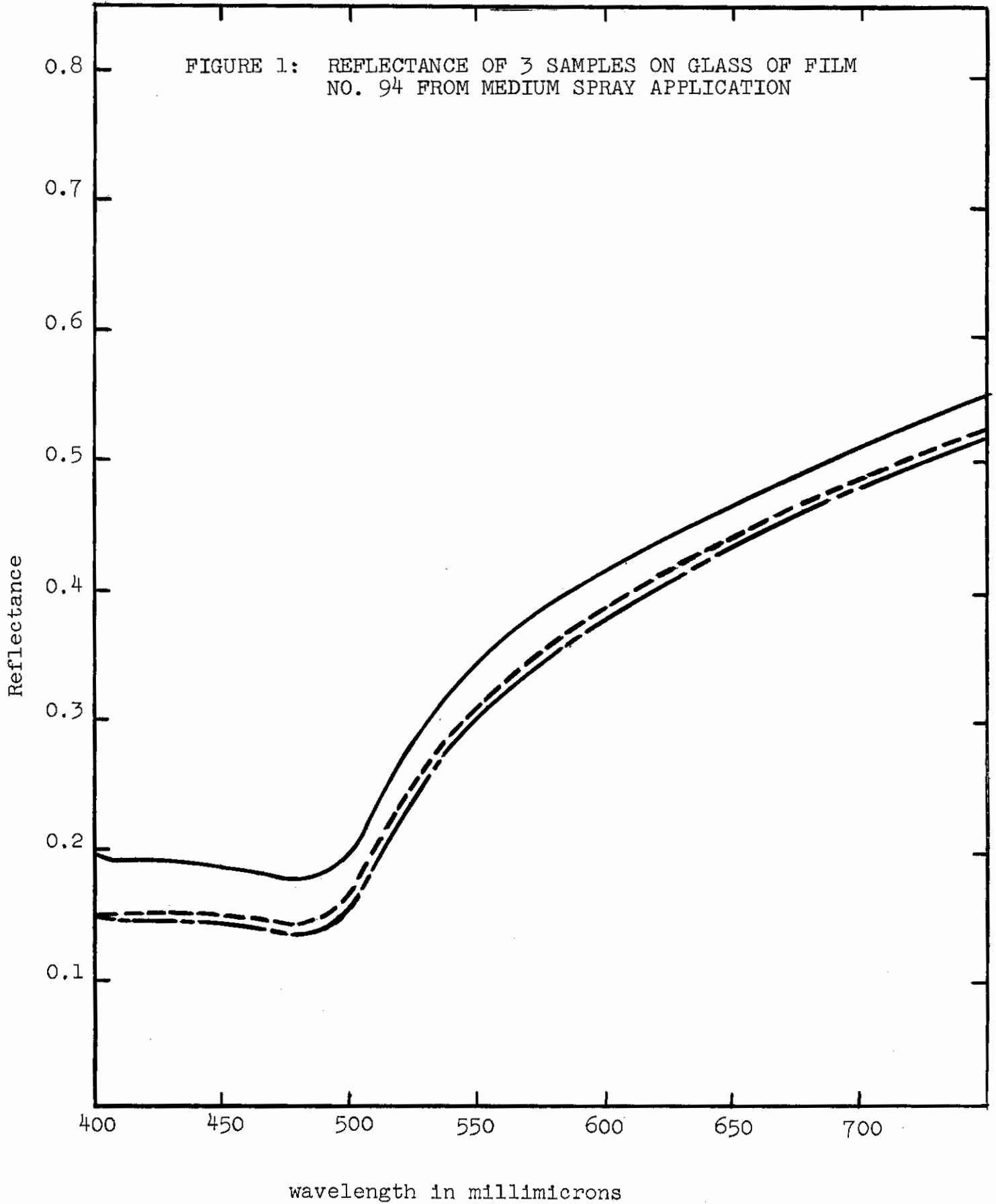
V FUTURE PROGRAM

Information developed in Parts I and II of this research provides the designer with a solar energy absorbing surface which is easily fabricated and which is stable at elevated temperatures in a vacuum equivalent to that found in space. Further research in this area is not recommended.

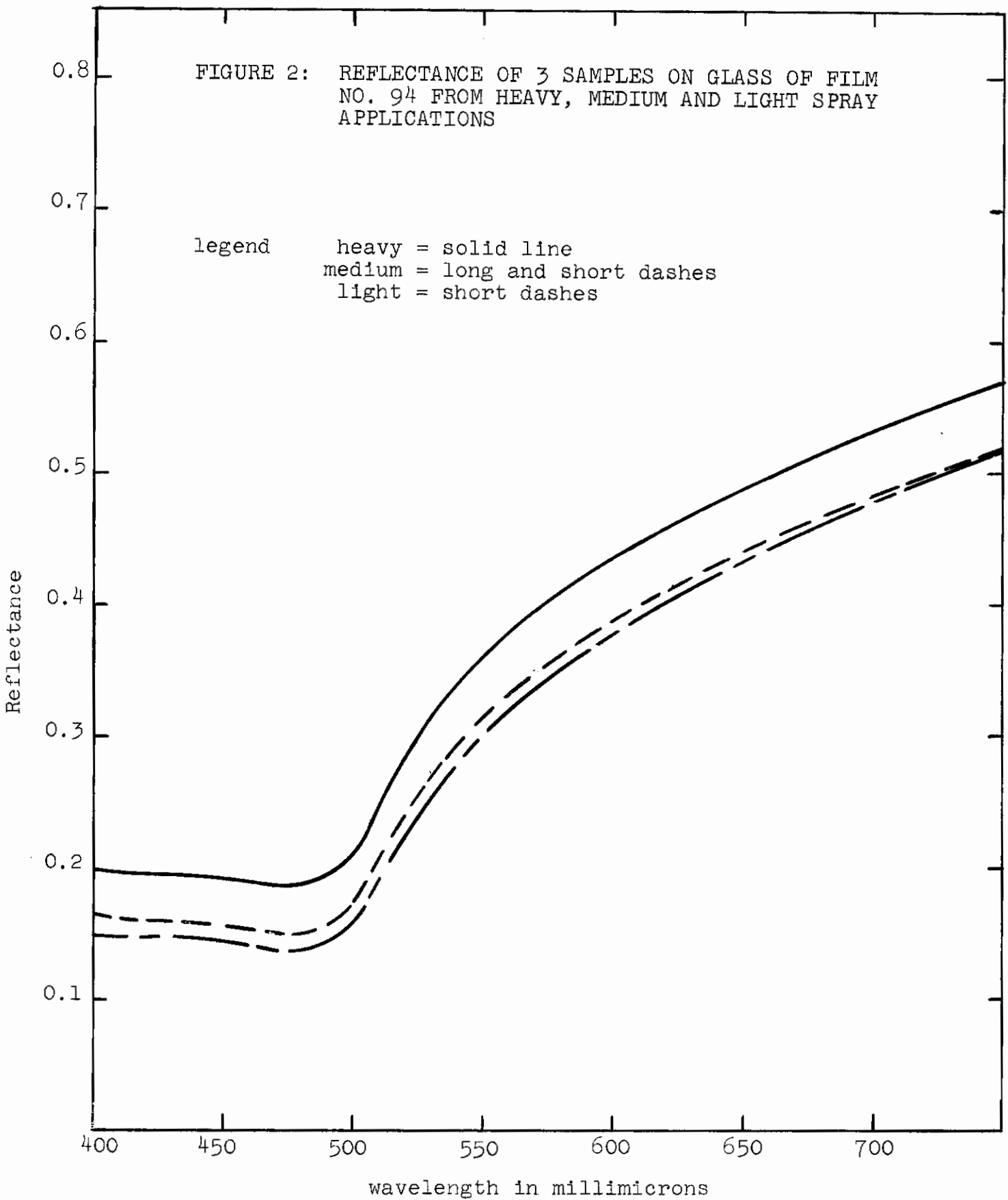
The investigation demonstrated that very thin oxide films can be easily obtained by spraying properly formulated organic solutions and firing in air. In contrast to techniques such as sputtering and vapor deposition of thin films, this area is relatively unexplored. The potential of using such thin oxide films in a variety of applications might be investigated. The ease of application of organic solutions could result in more versatile and less costly techniques than the vacuum methods now widely used in coating fabrication.

VI LIST OF REFERENCES

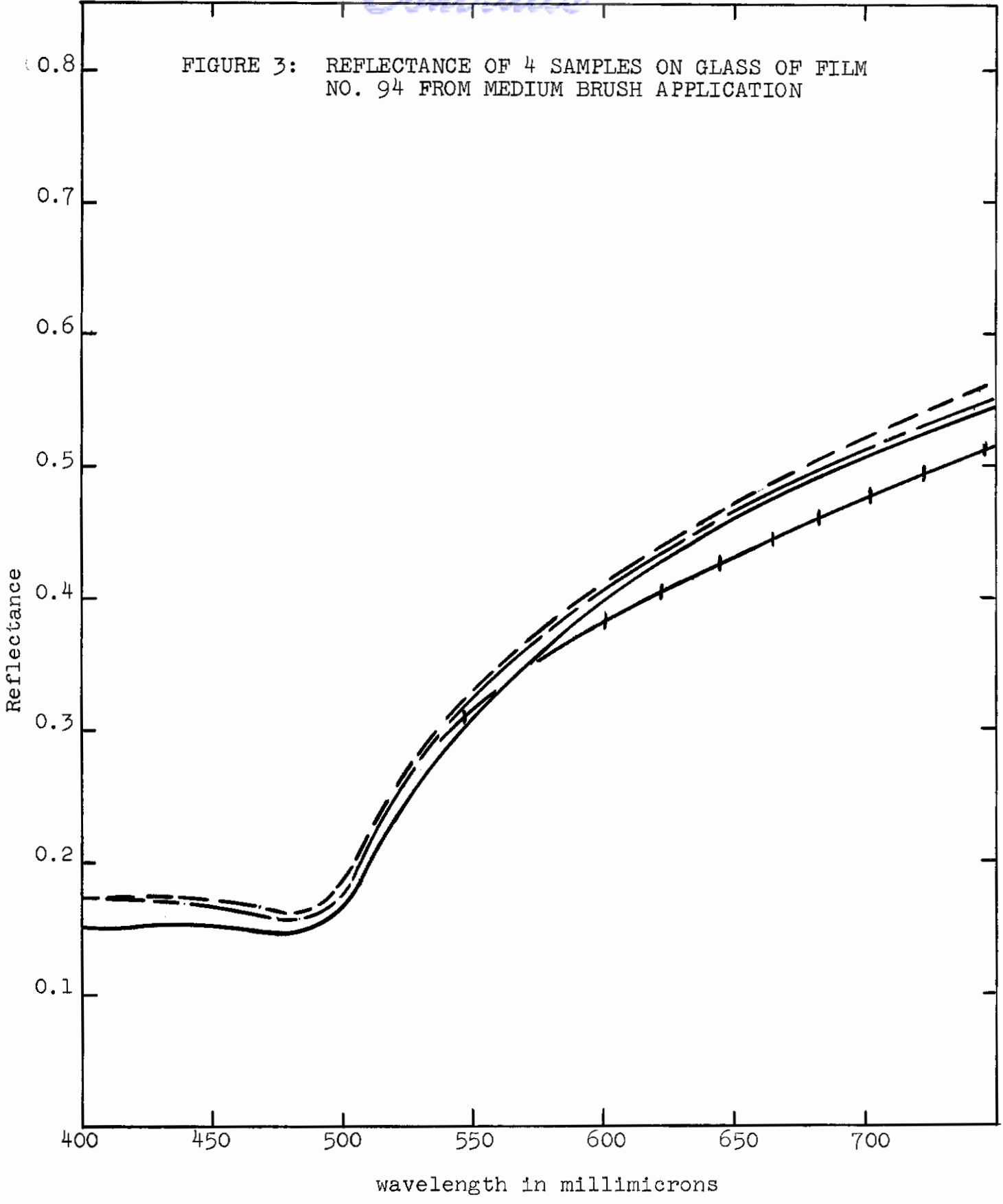
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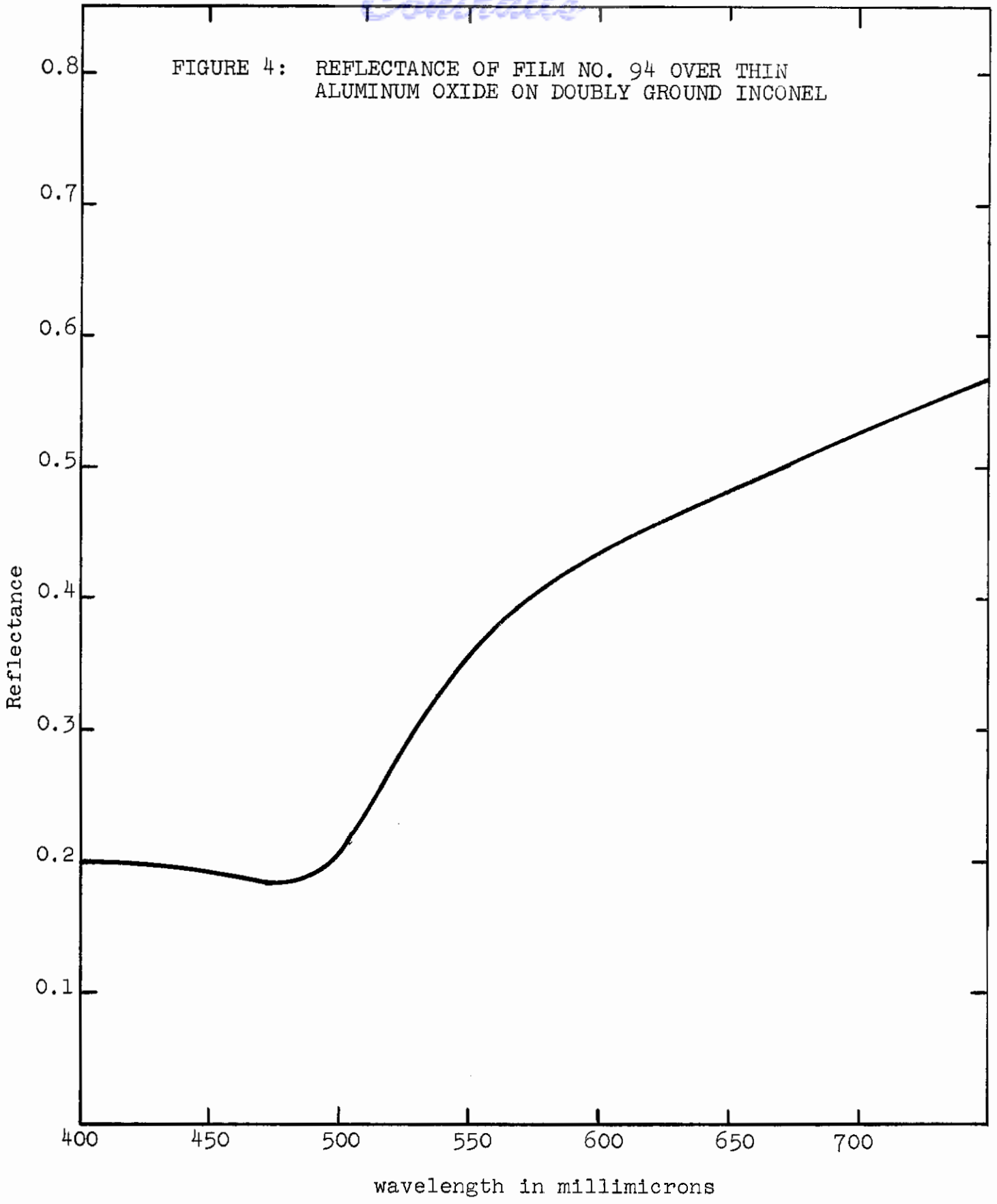


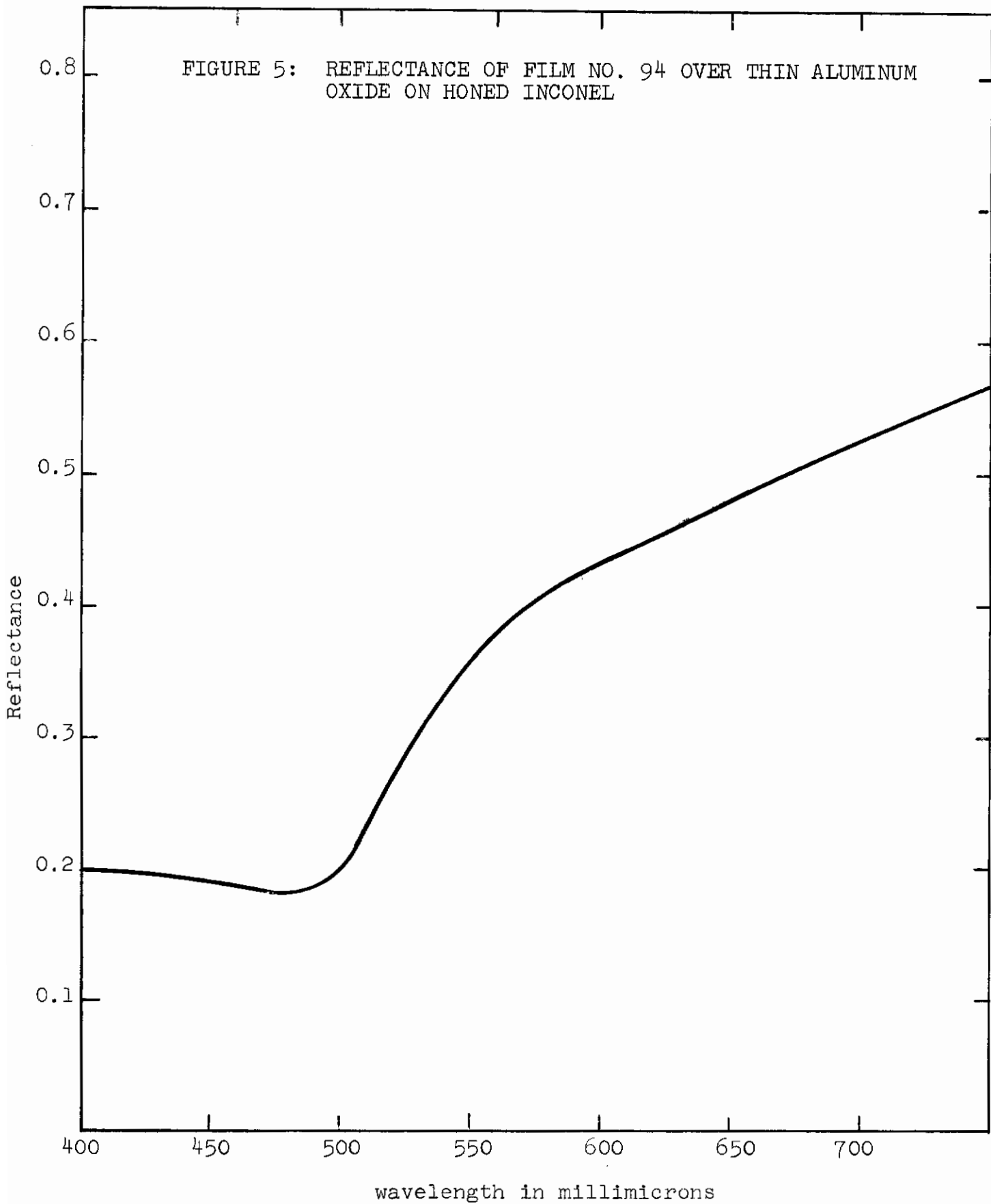
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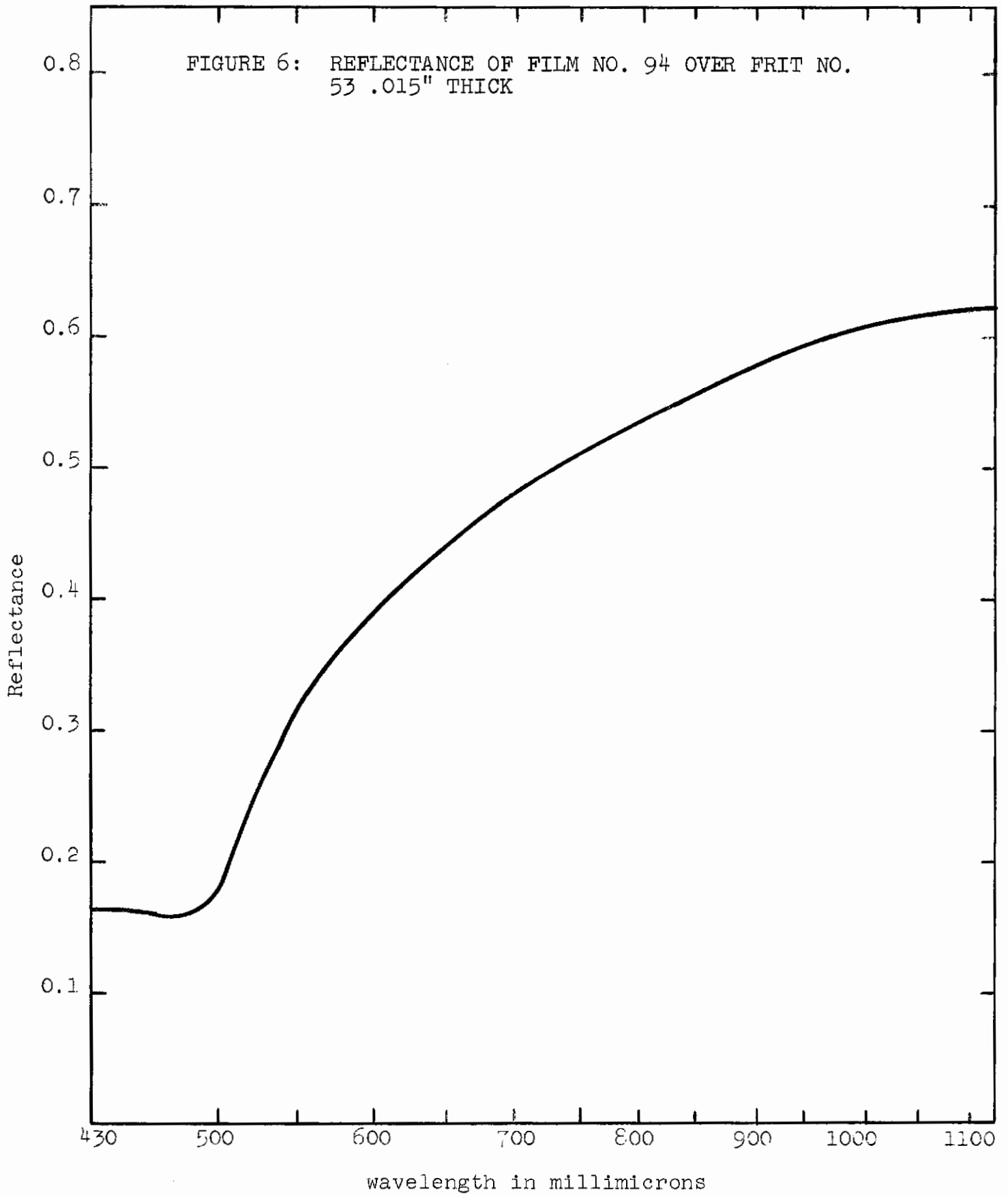


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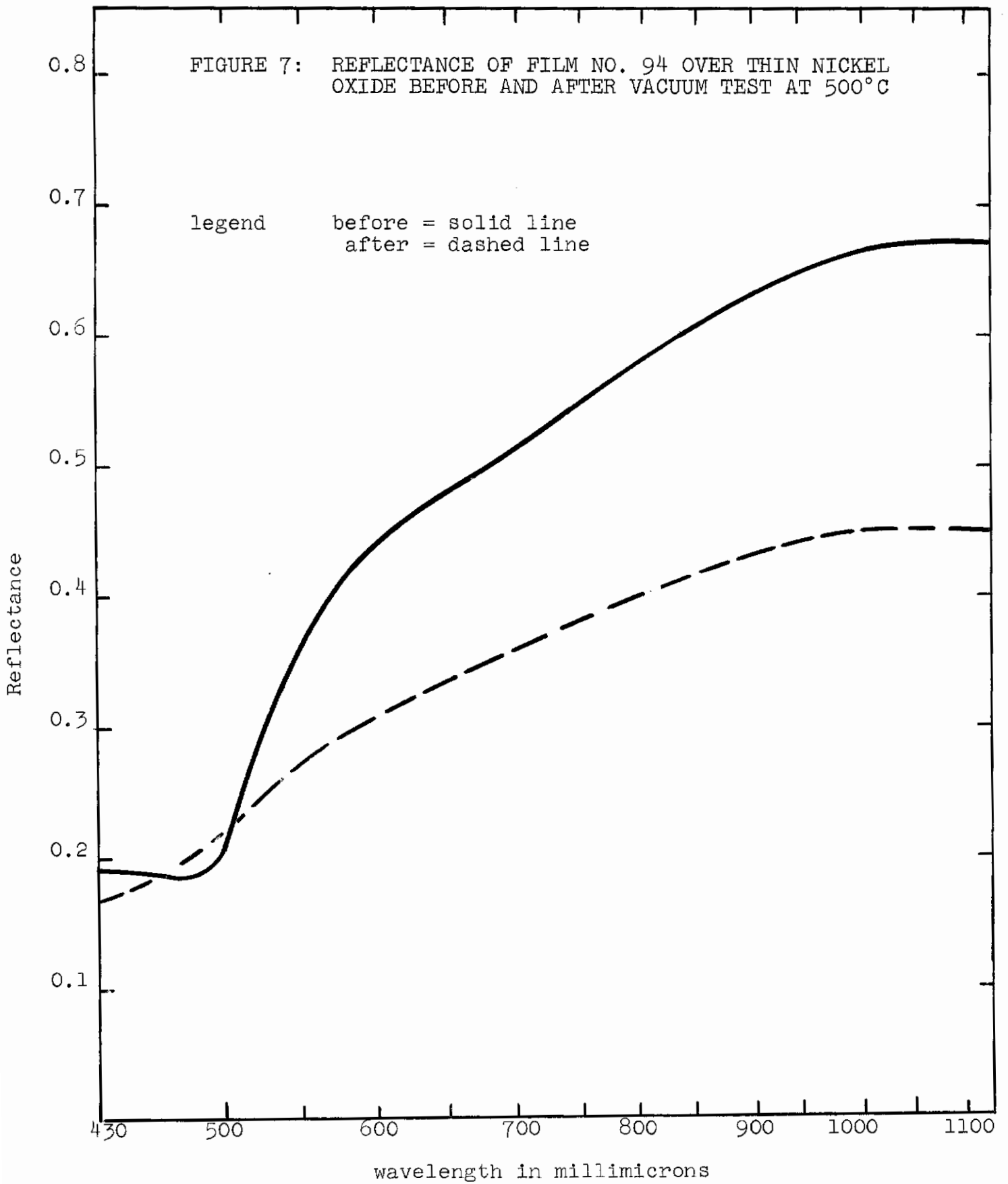
FIGURE 4: REFLECTANCE OF FILM NO. 94 OVER THIN ALUMINUM OXIDE ON DOUBLY GROUND INCONEL

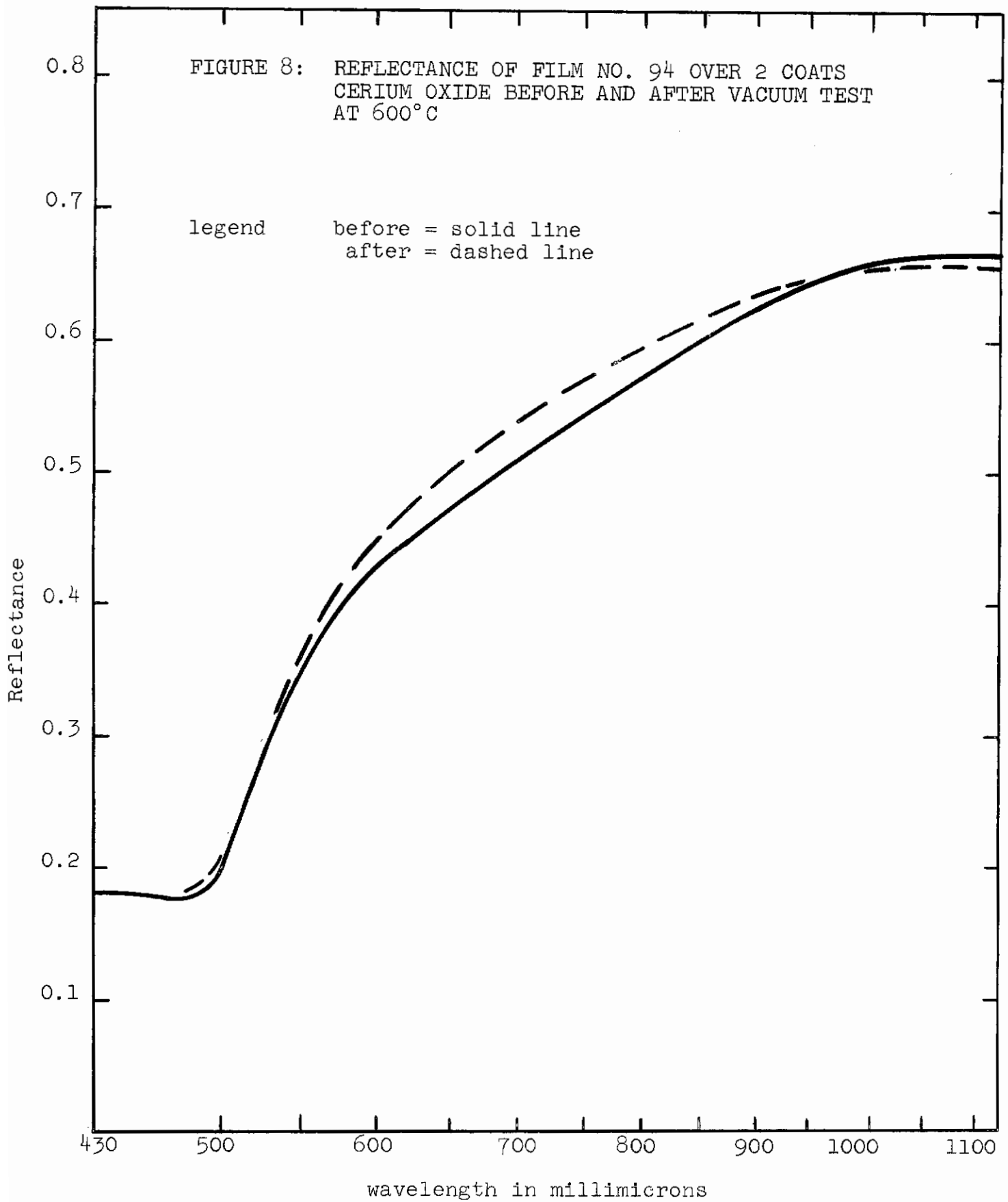


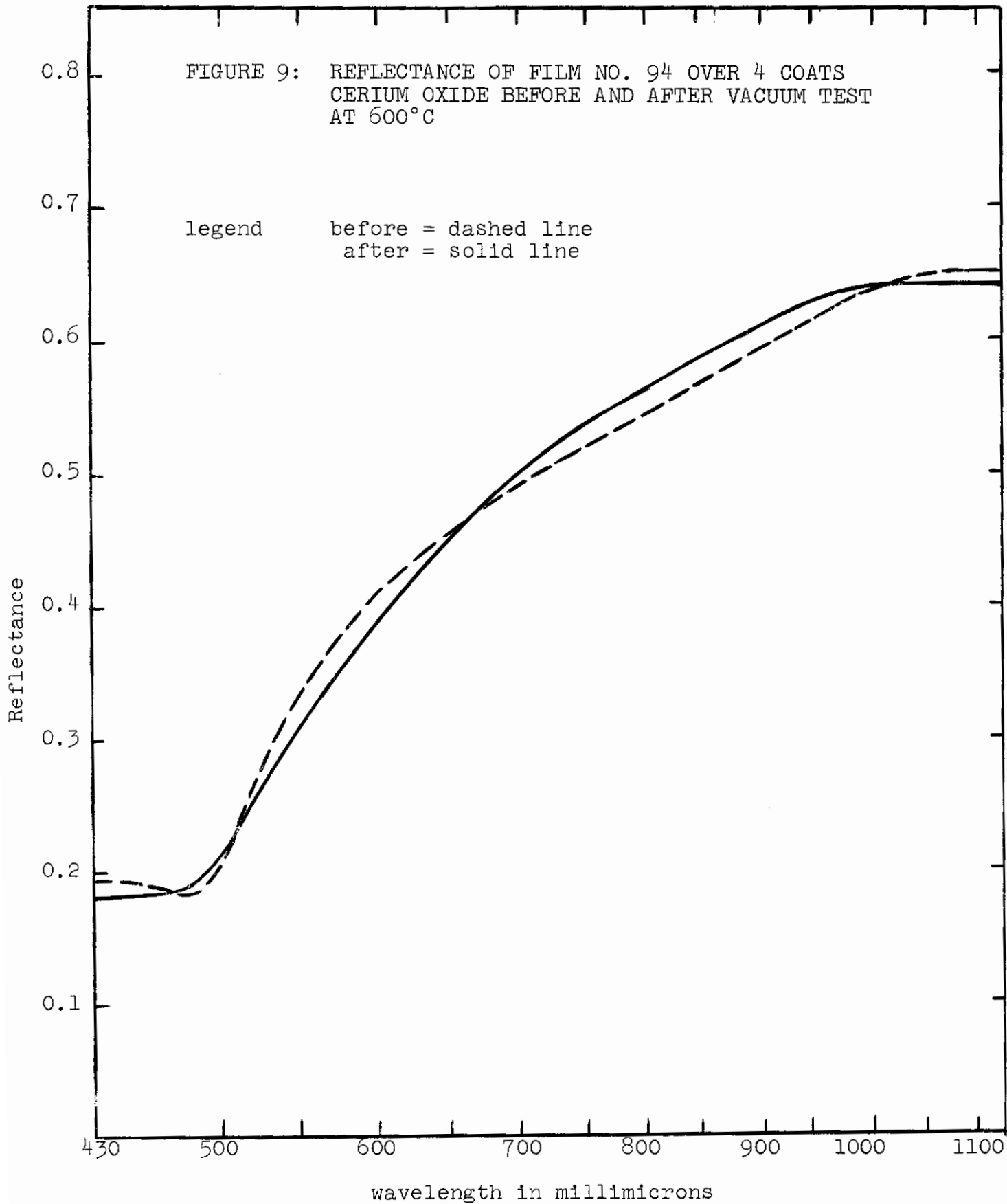


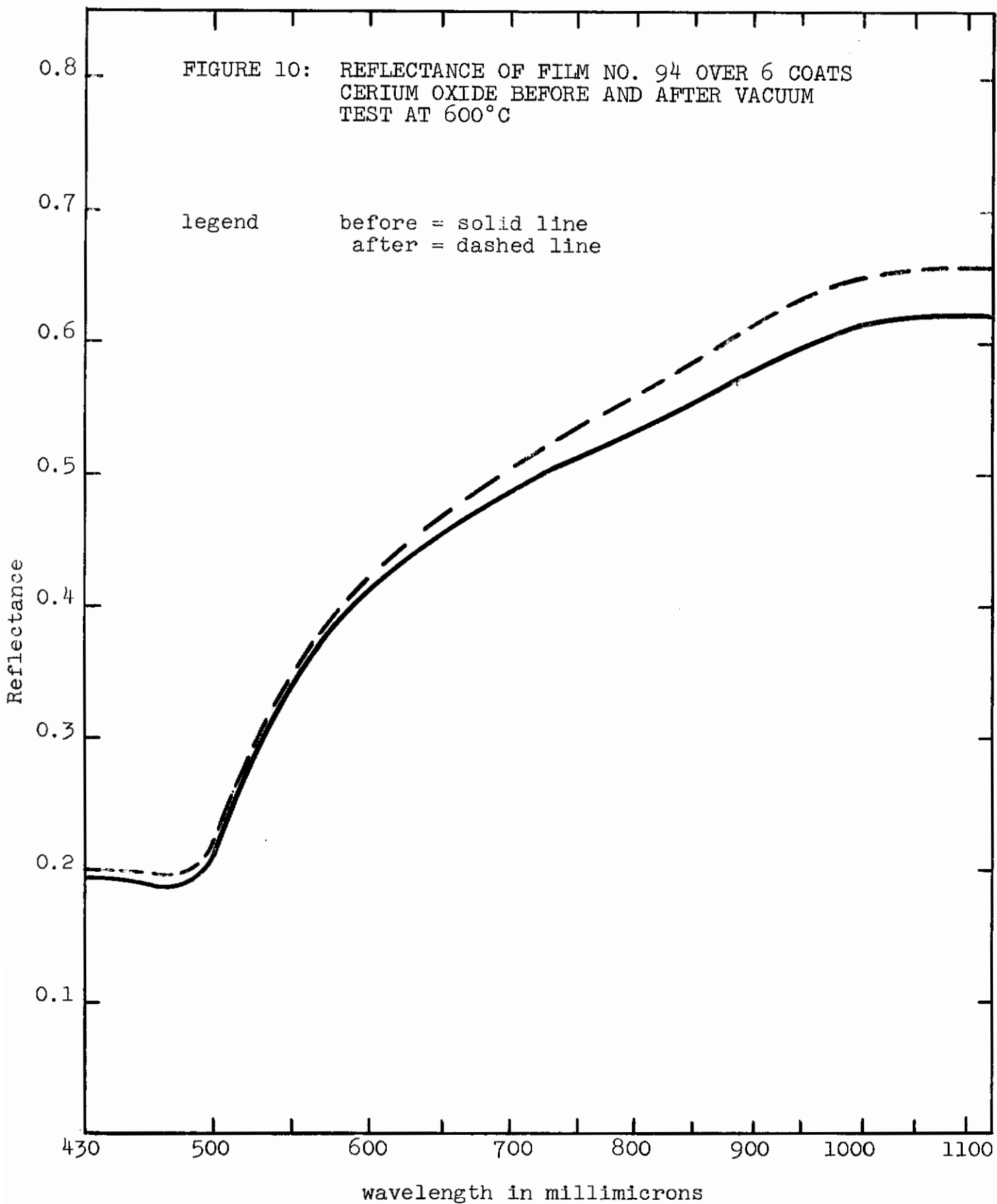


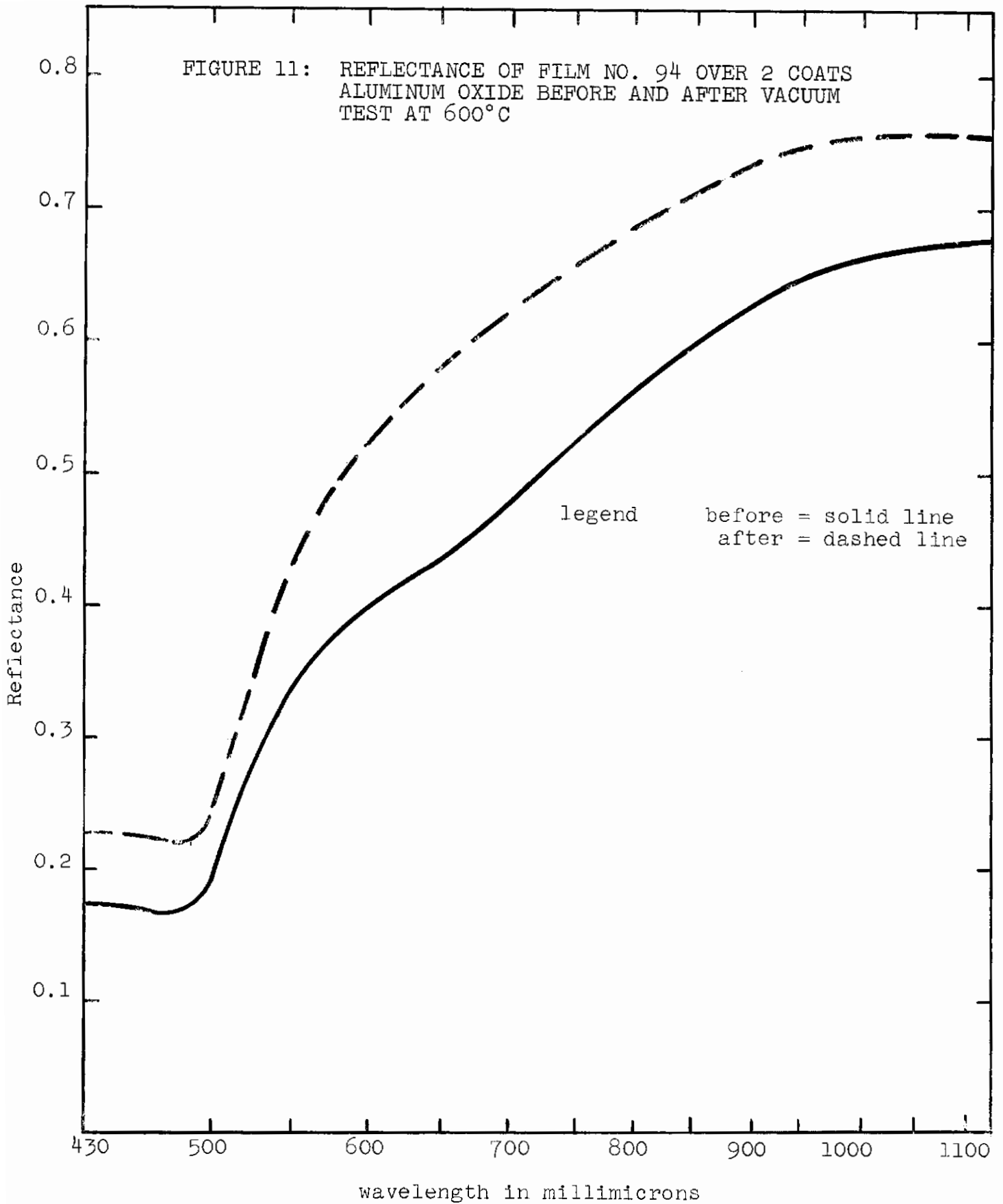
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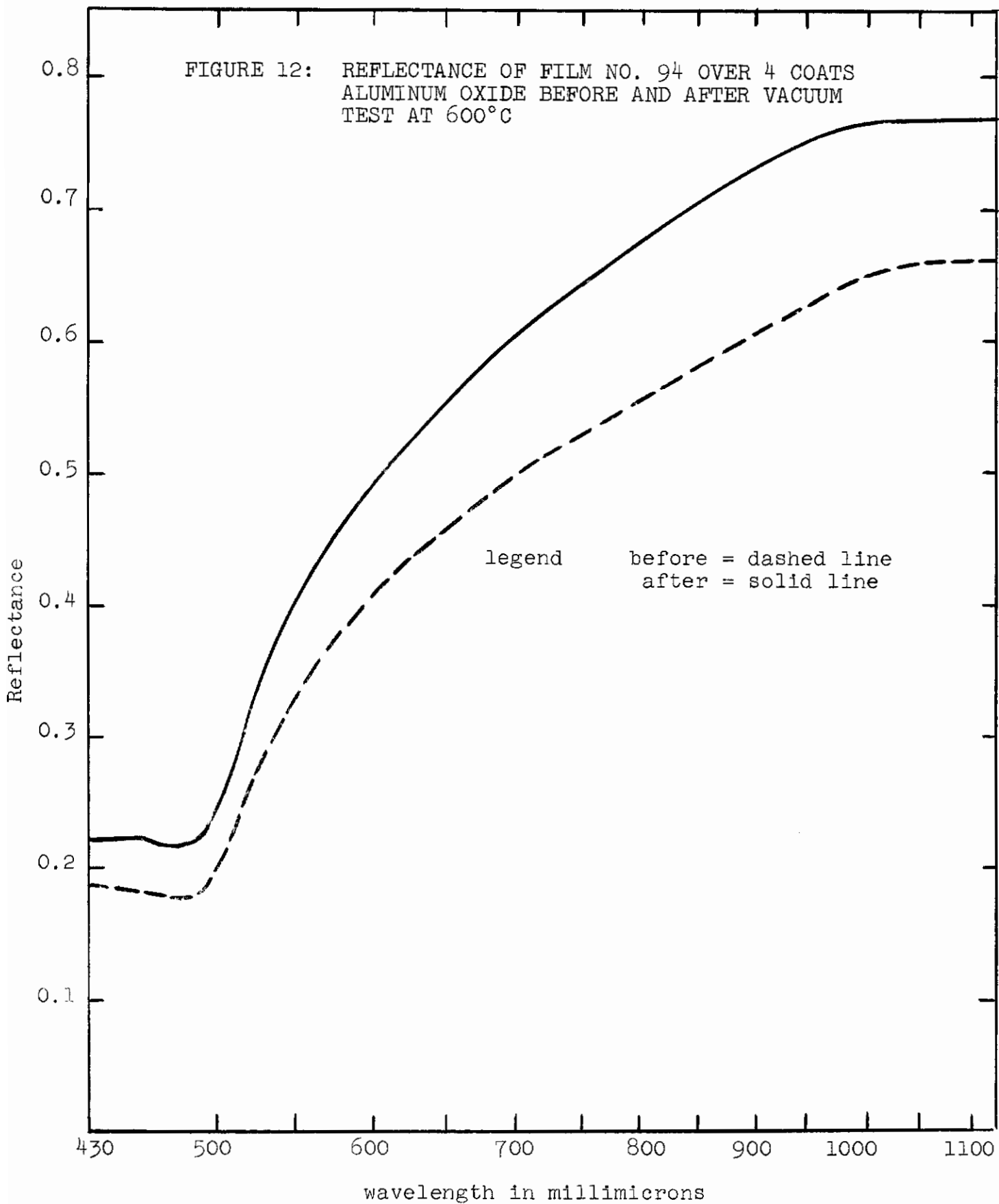












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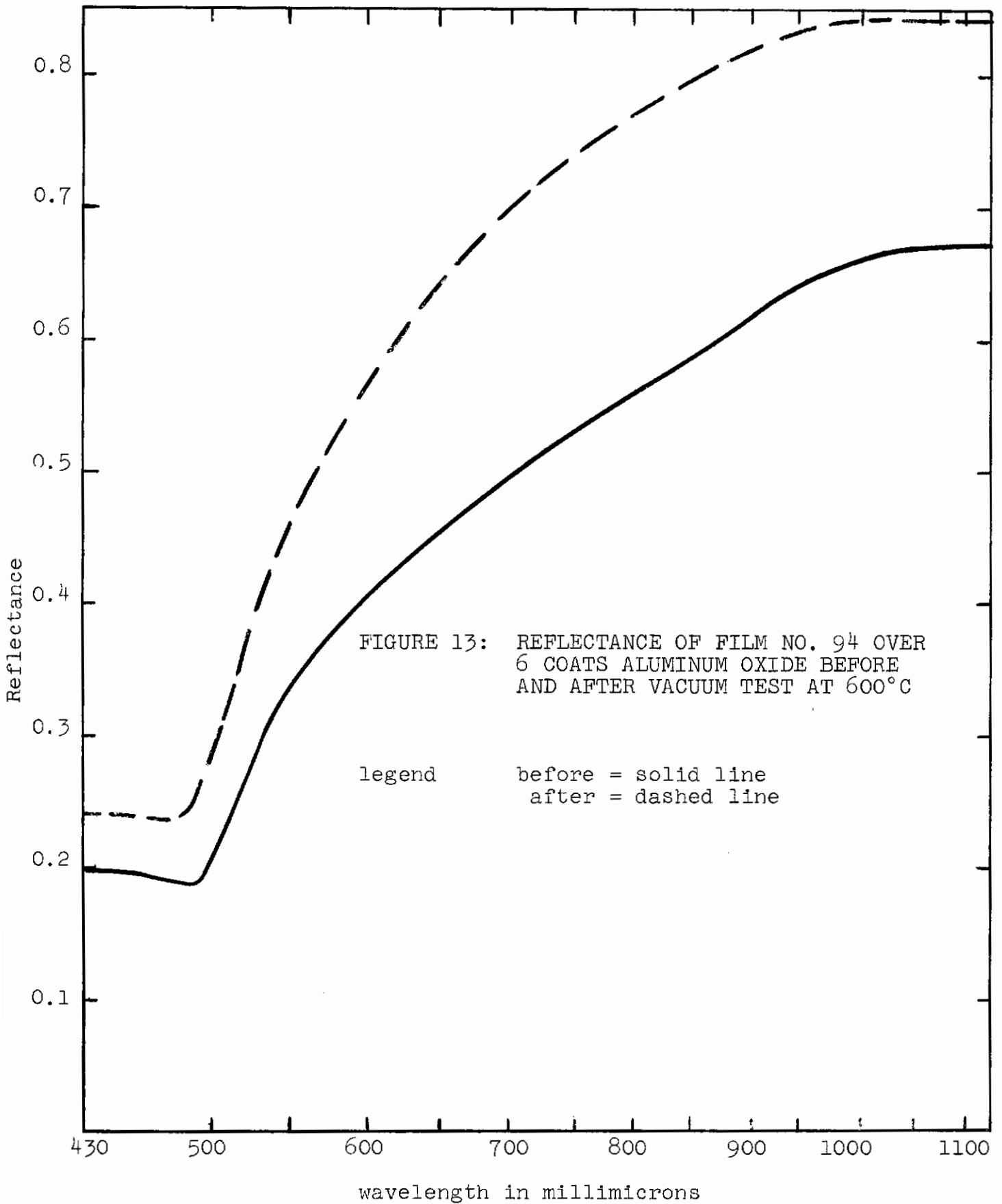
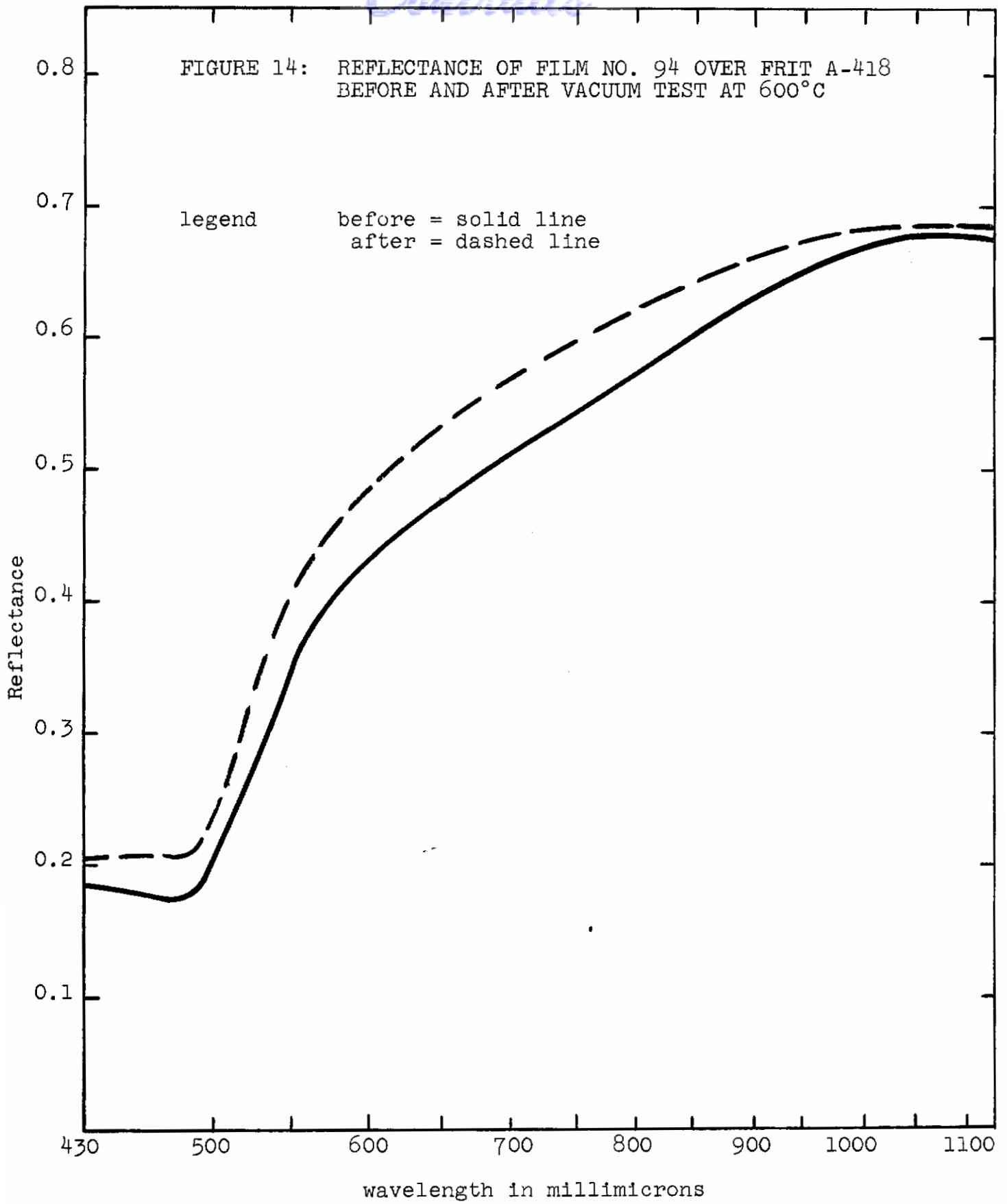


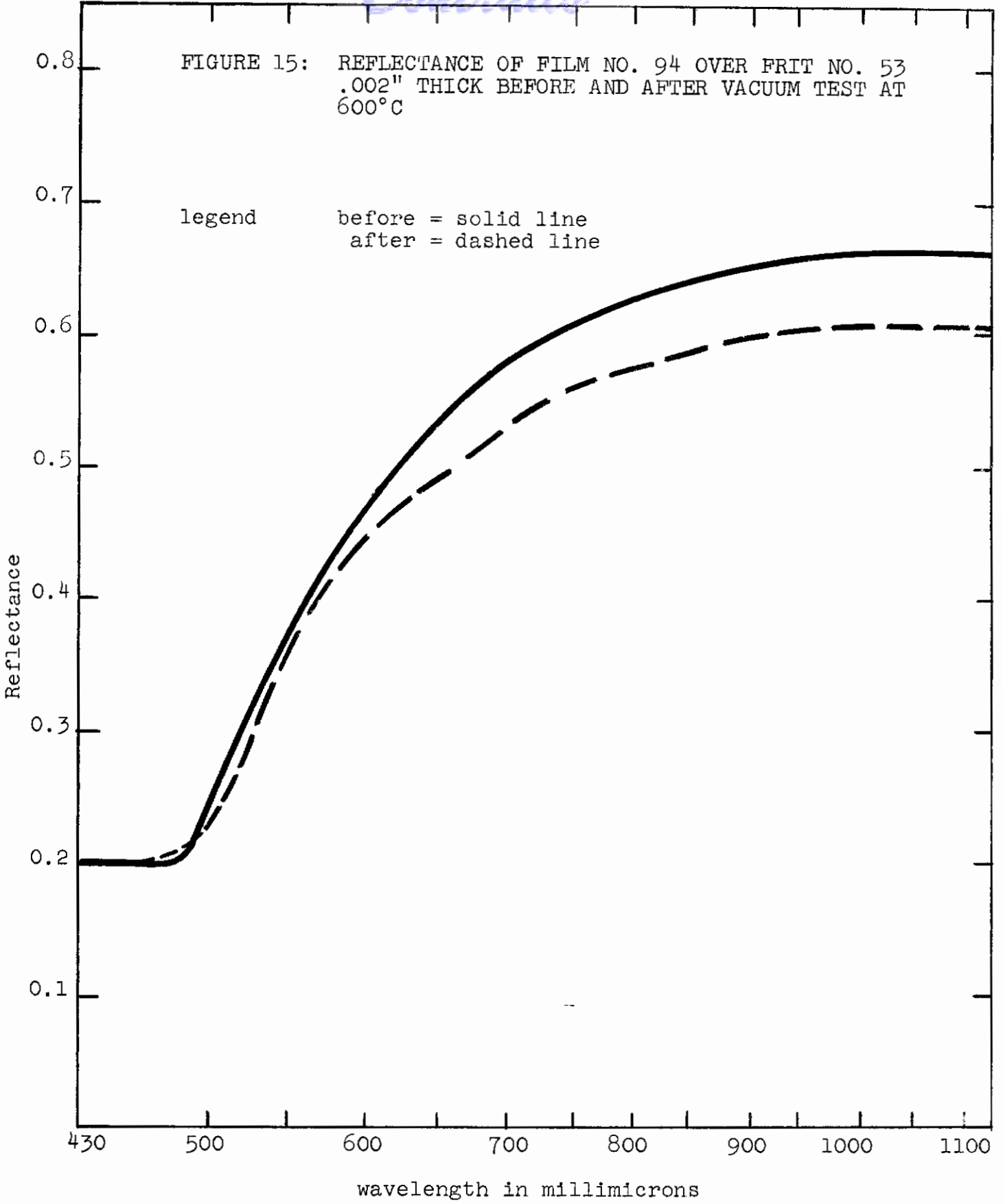
FIGURE 13: REFLECTANCE OF FILM NO. 94 OVER 6 COATS ALUMINUM OXIDE BEFORE AND AFTER VACUUM TEST AT 600°C

legend before = solid line
 after = dashed line

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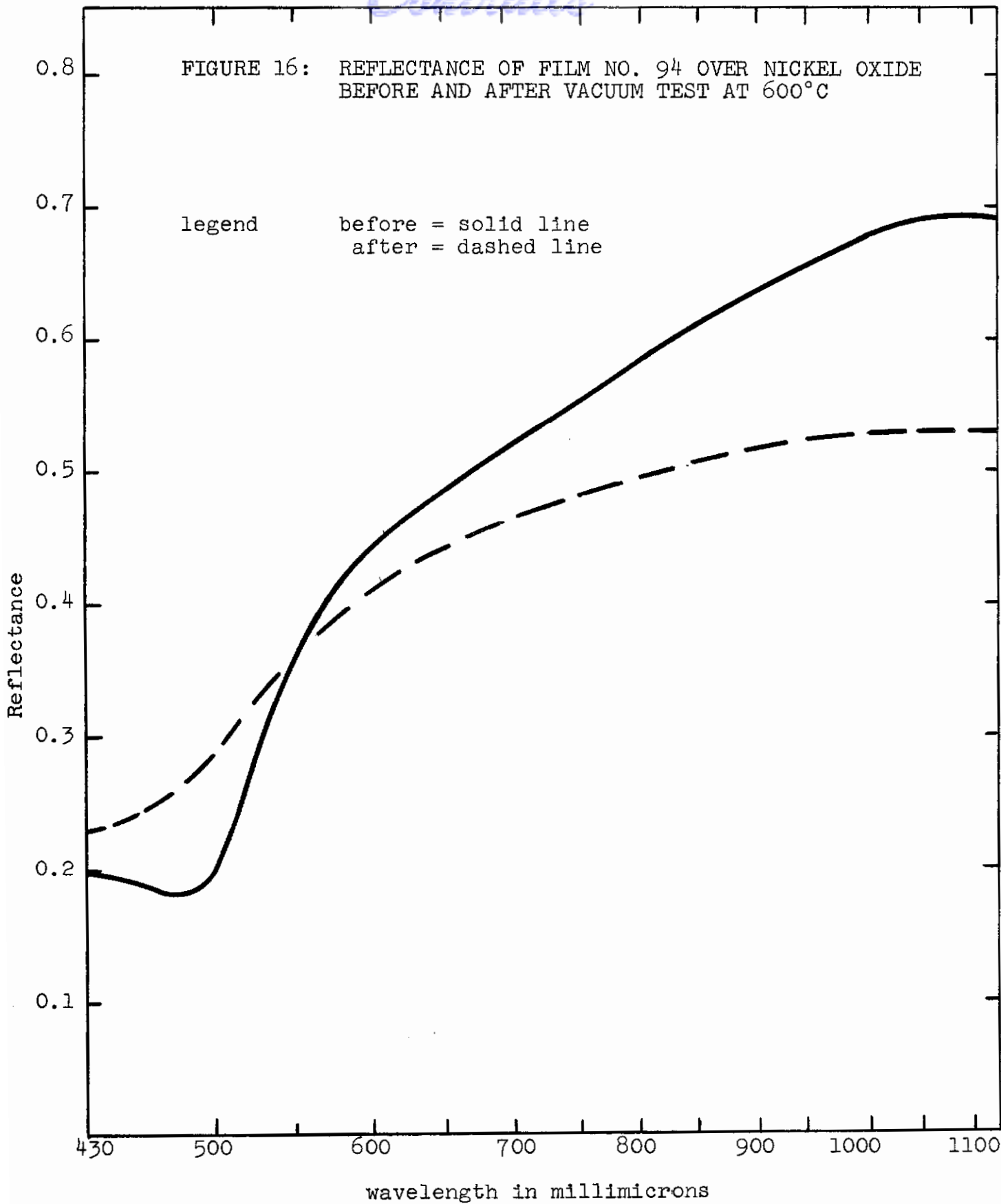


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FIGURE 16: REFLECTANCE OF FILM NO. 94 OVER NICKEL OXIDE BEFORE AND AFTER VACUUM TEST AT 600°C



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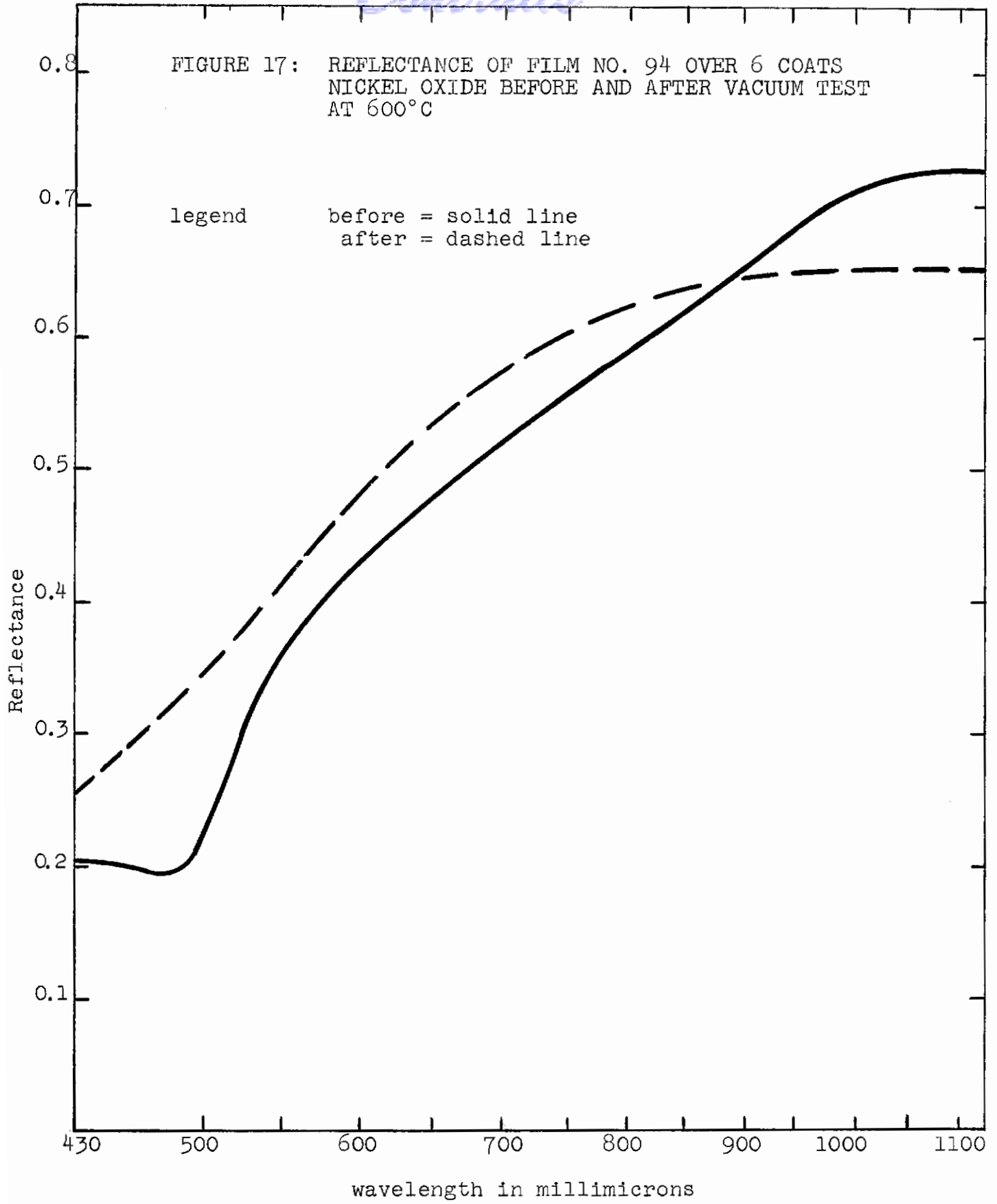
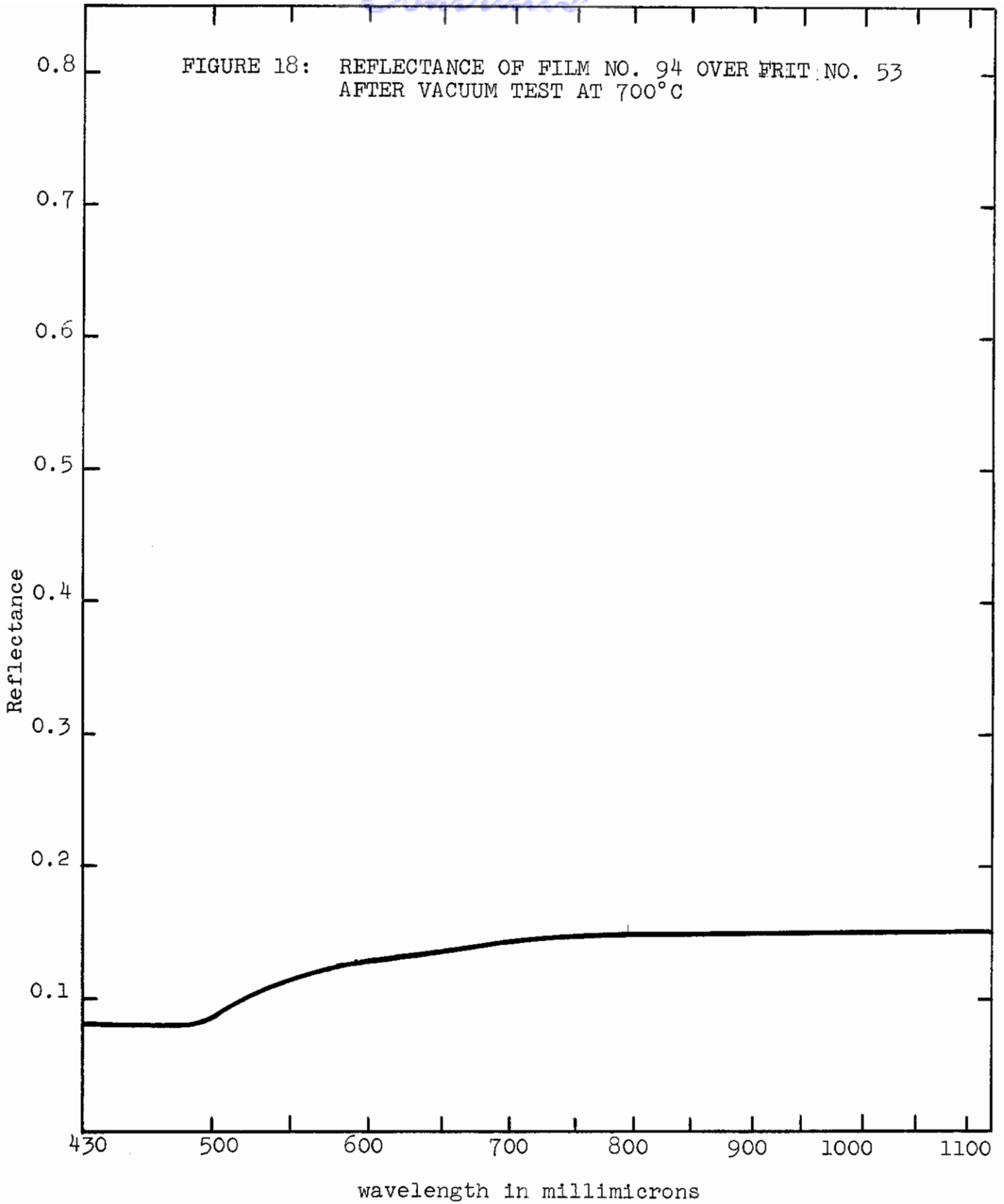


FIGURE 18: REFLECTANCE OF FILM NO. 94 OVER FRIT: NO. 53
AFTER VACUUM TEST AT 700°C



Continuity

FIGURE 19: REFLECTANCE OF FILM NO. 94 OVER FRIT A-418
AFTER VACUUM TEST AT 700°C

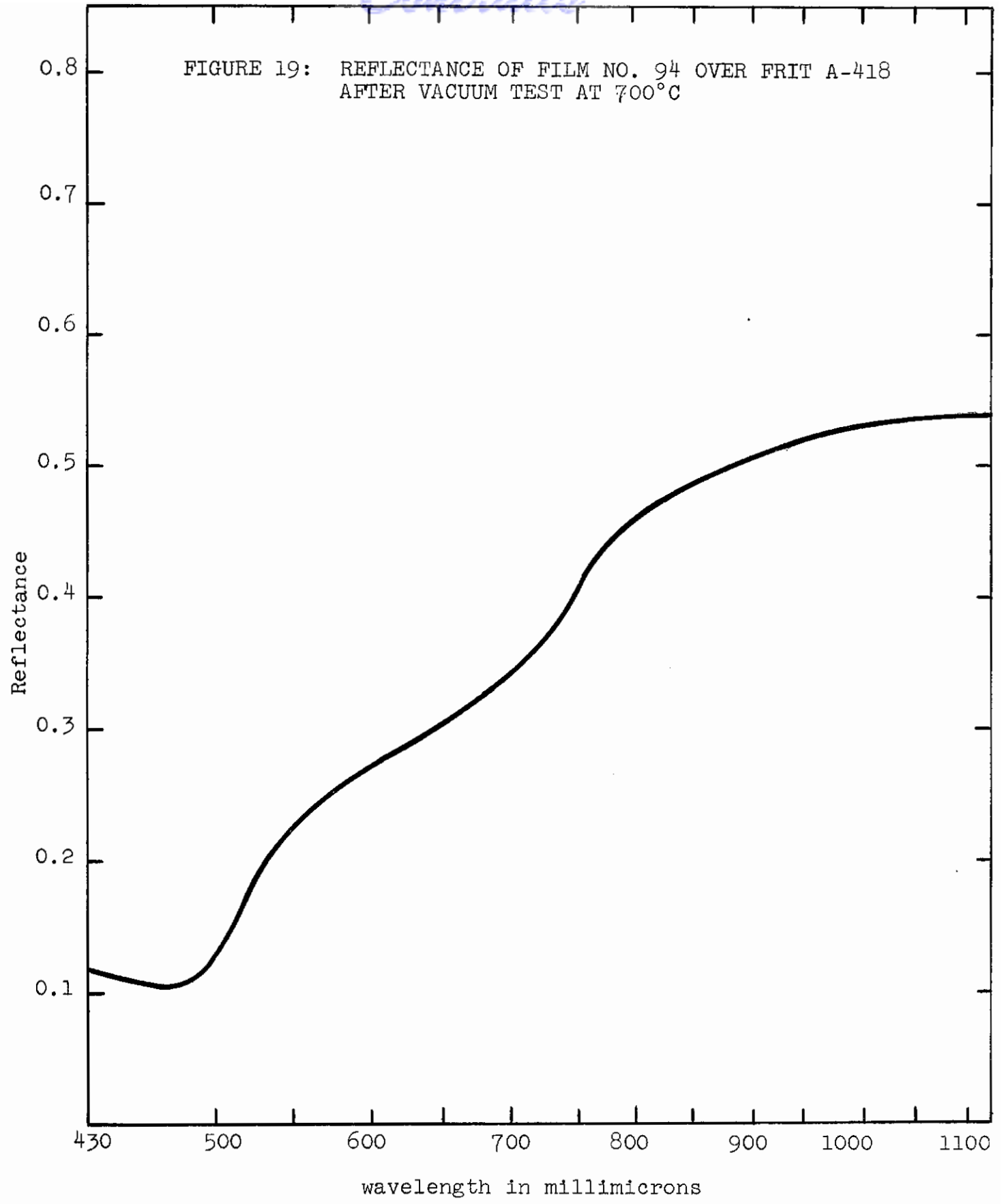
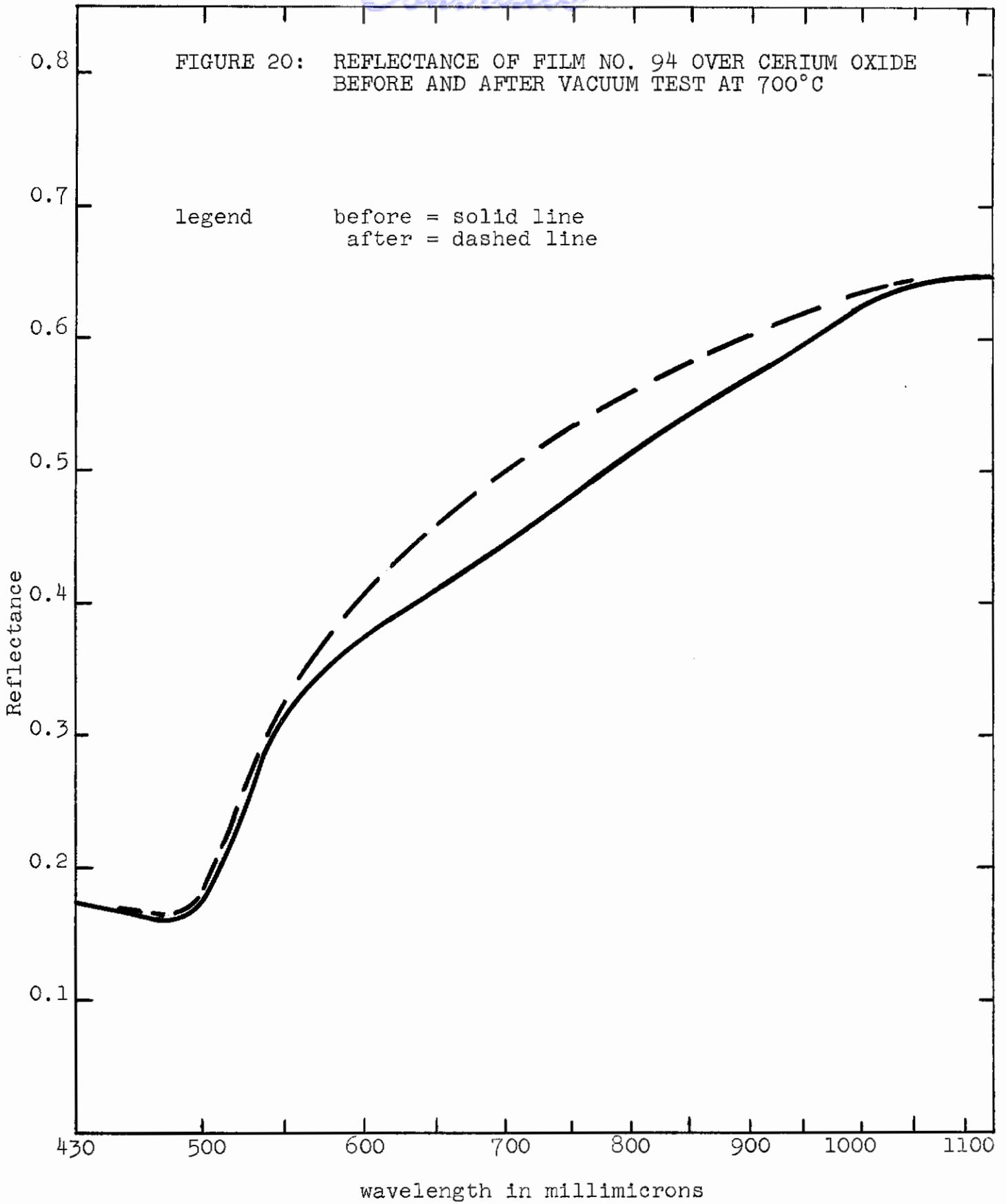
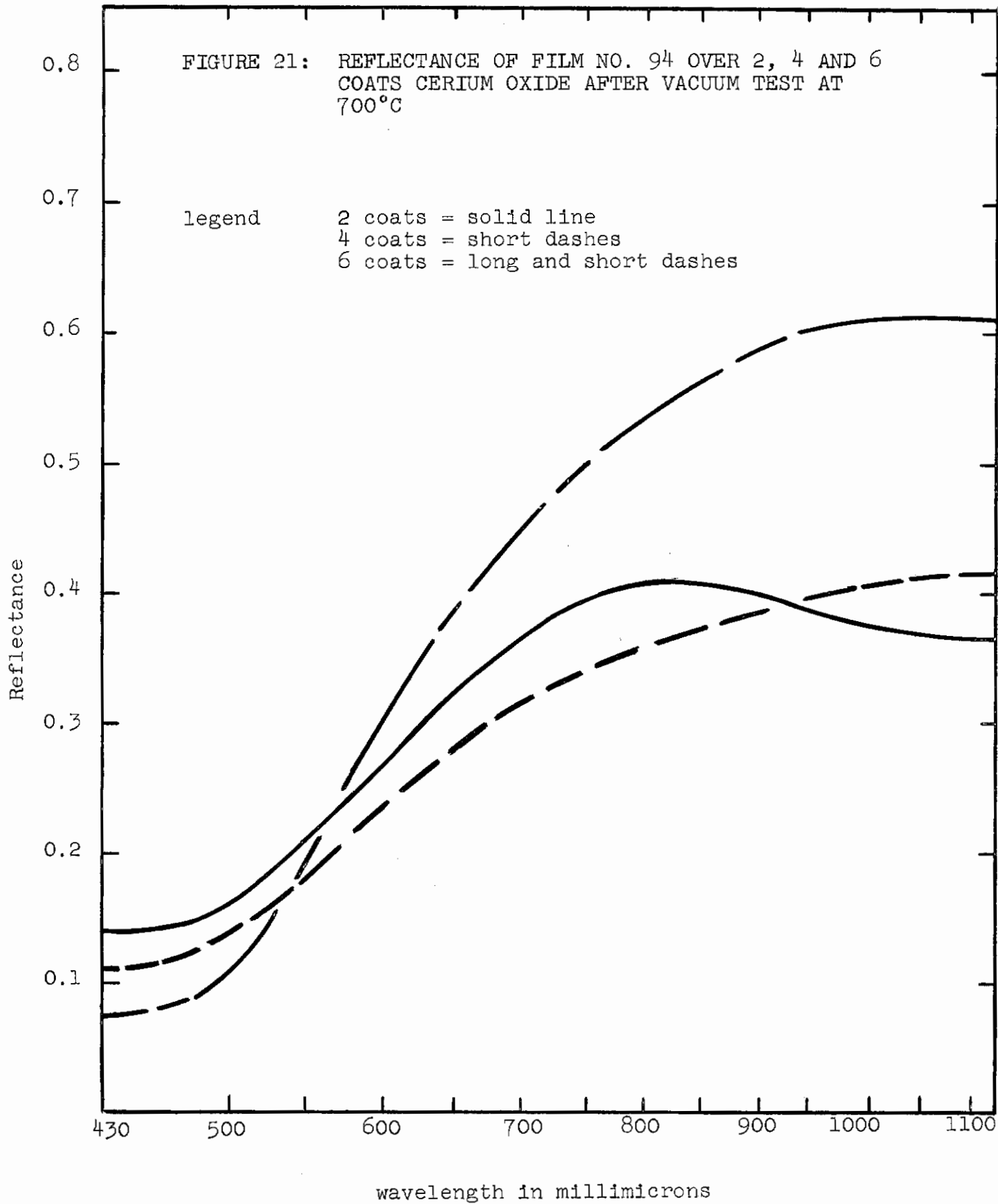


FIGURE 20: REFLECTANCE OF FILM NO. 94 OVER CERIUM OXIDE BEFORE AND AFTER VACUUM TEST AT 700°C



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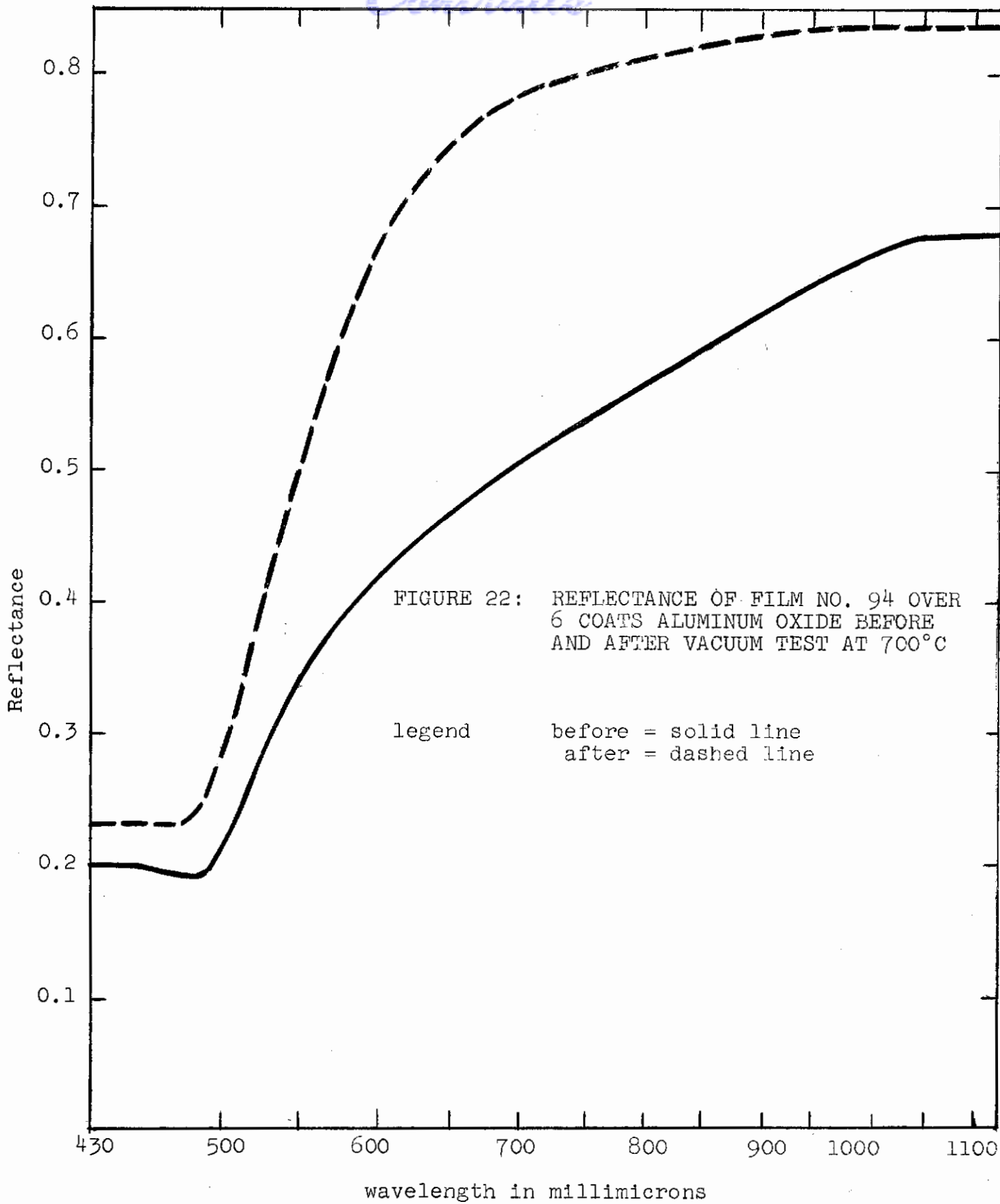


FIGURE 22: REFLECTANCE OF FILM NO. 94 OVER 6 COATS ALUMINUM OXIDE BEFORE AND AFTER VACUUM TEST AT 700°C

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 after = dashed line

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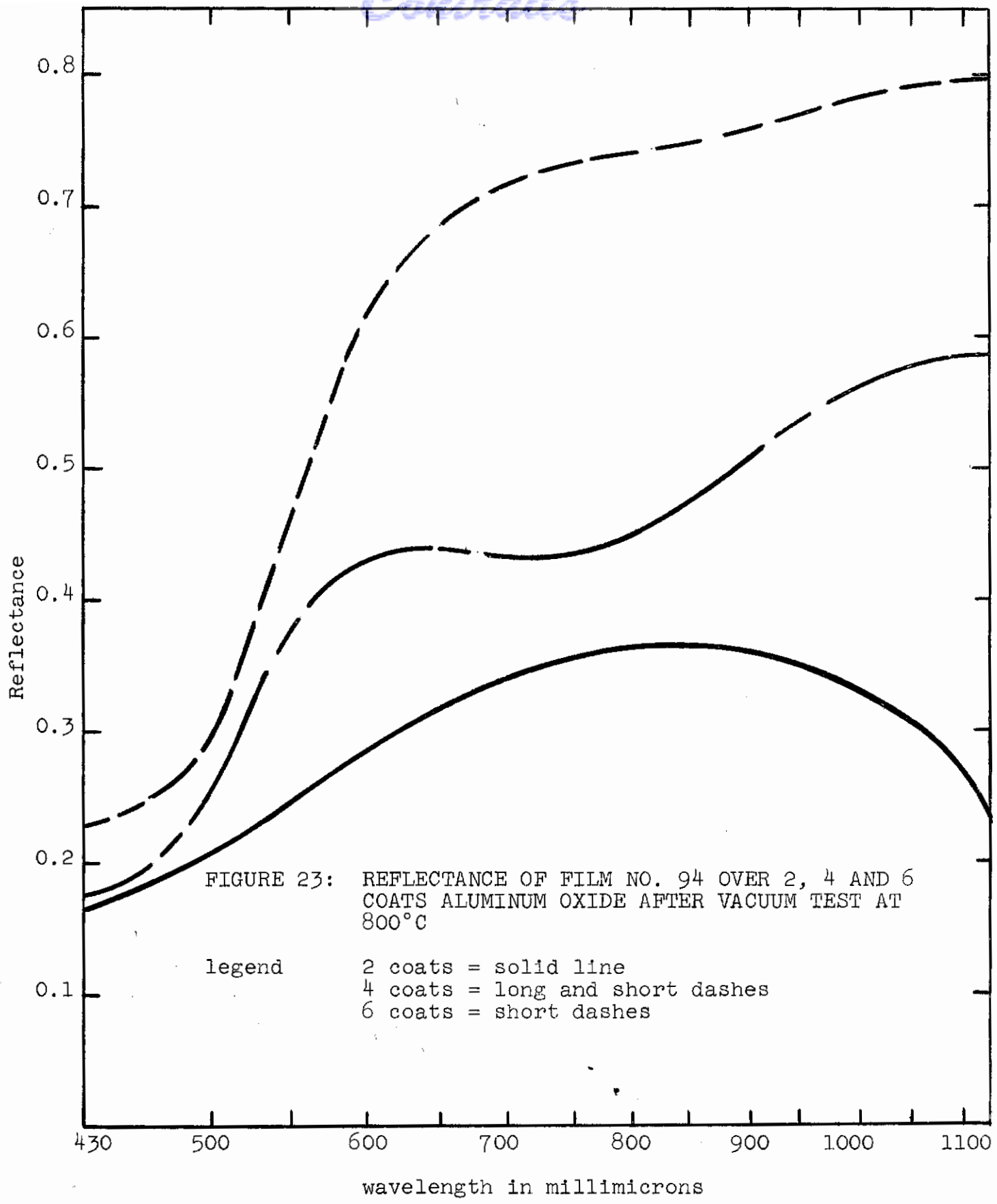
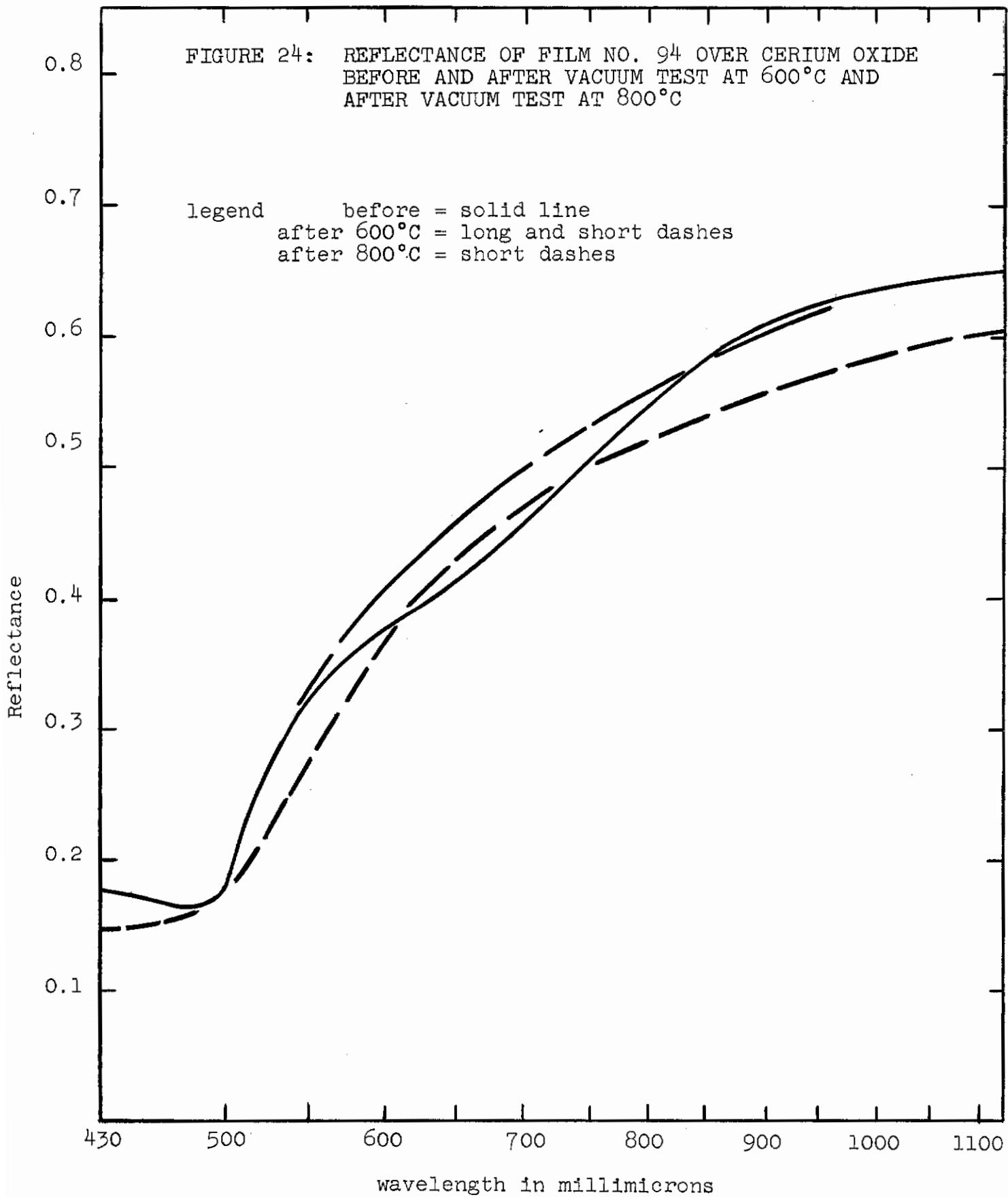
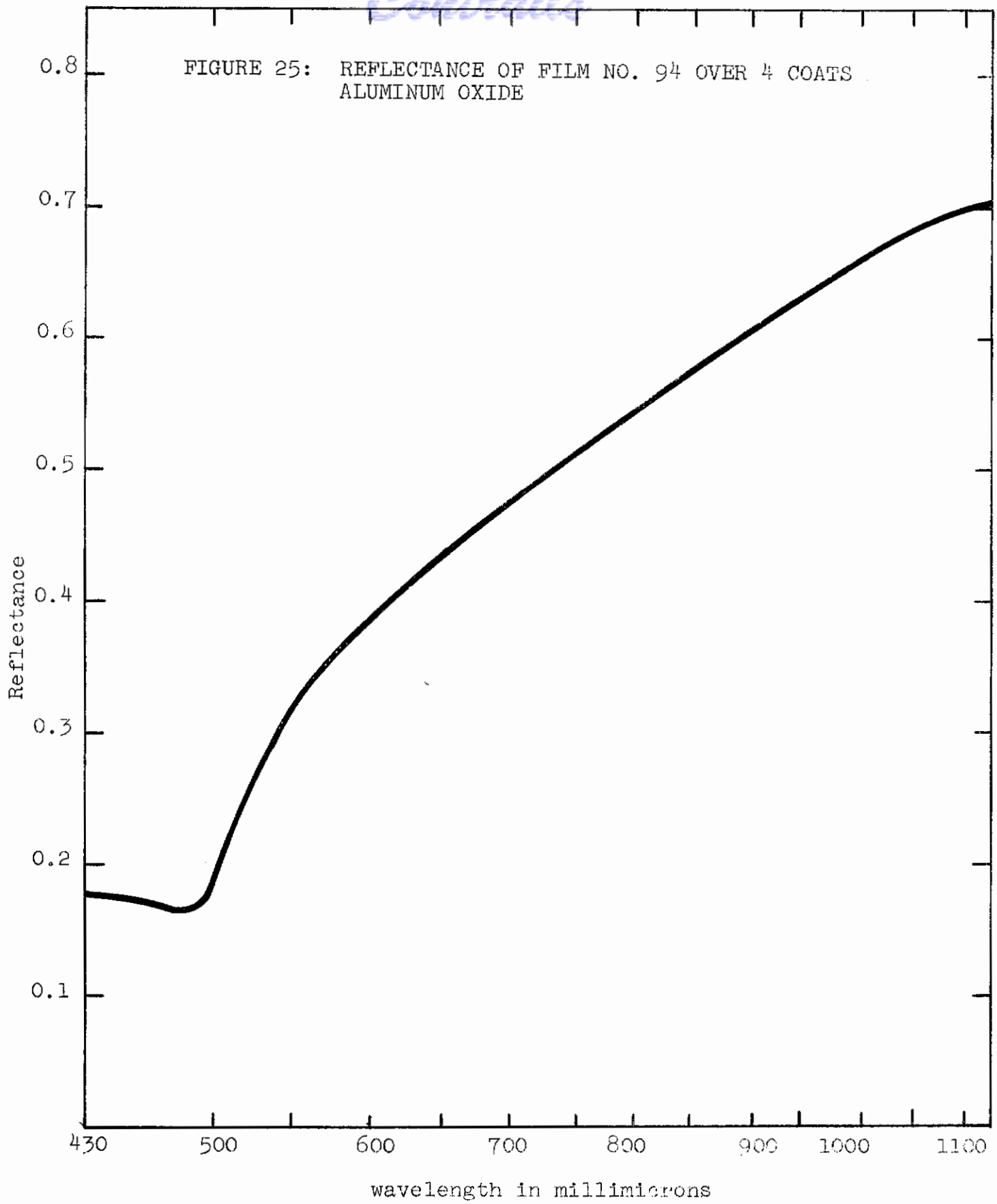


FIGURE 23: REFLECTANCE OF FILM NO. 94 OVER 2, 4 AND 6 COATS ALUMINUM OXIDE AFTER VACUUM TEST AT 800°C

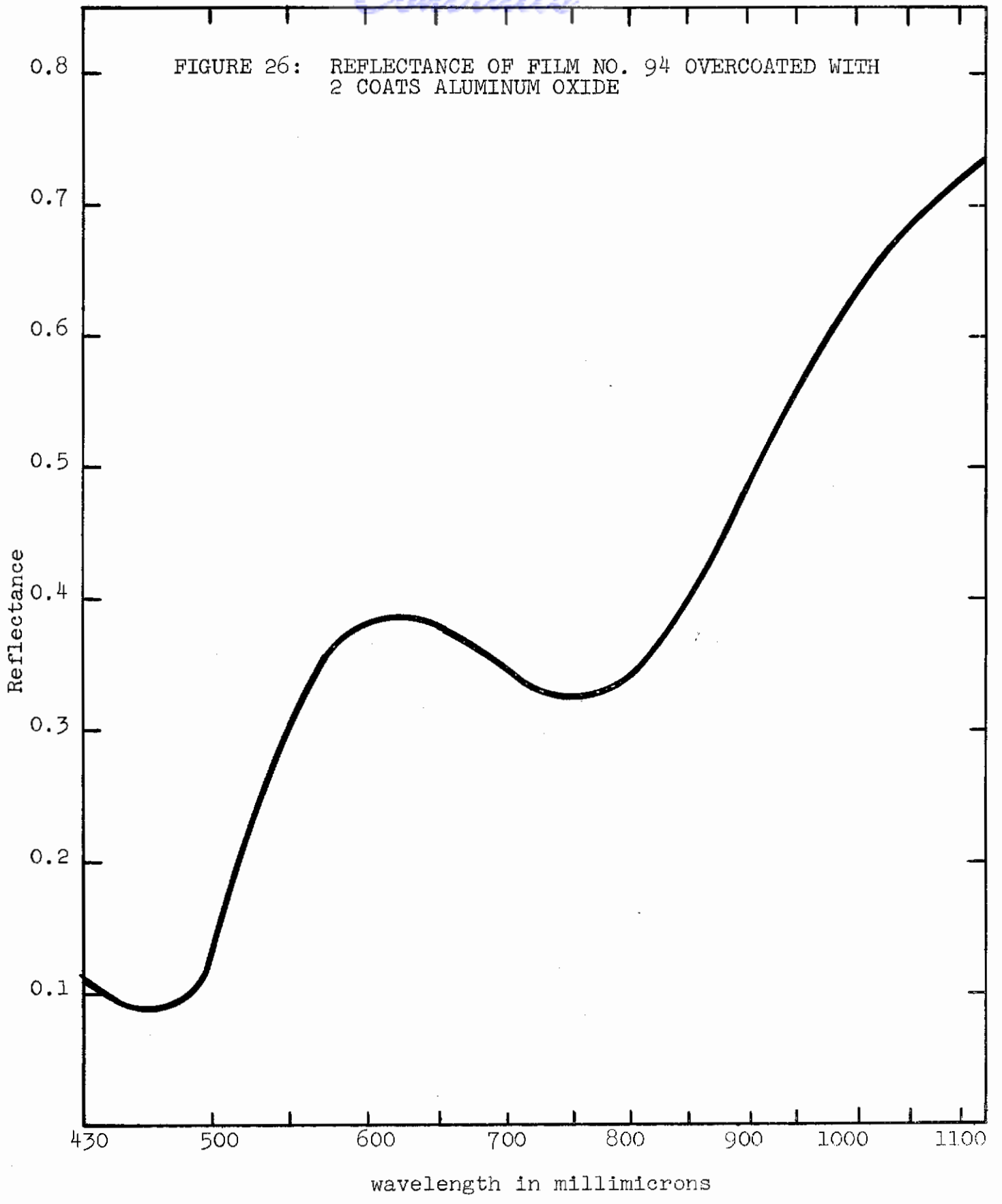
legend
2 coats = solid line
4 coats = long and short dashes
6 coats = short dashes



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FIGURE 27: REFLECTANCE OF FILM NO. 94 ON FRIT A-418
VERSUS POLISHED ALUMINUM STANDARD

