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NAVAL RESEARCH LABORATORY
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CHEMISTRY DIVISION - HIGH POLYMER SECTION

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THREE-LAYER REFLECTION-REDUCING COATINGS FOR OPTICAL ELEMENTS

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ABSTRACT

An investigation has been made of three-layered reflection-reducing films similar in principle to those recently developed in Germany. Very effective coatings have been produced by use of materials of the type developed by the American Optical Company. The maximum expected reduction in reflection has not been obtained, however, because none of the available materials has a high enough refractive index.

The difficulty involved in the preparation of the coatings probably makes them undesirable for general use but they may be suitable for special uses where the greatest possible reduction in reflection is required. For the latter cases, it might be desirable to produce these coatings through use of an evaporation process similar to that now used to produce magnesium fluoride coatings or through a vapor-deposition process similar to the German one, since materials of higher index are available through these techniques and three-layered coatings of lower reflection are thus possible.

The three-layered reflection-reducing coatings produced through the use of the American Optical Company type solutions are sufficiently durable to withstand normal usage but they are not as resistant to abrasion as the best grade of evaporated magnesium fluoride coatings.

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I. INTRODUCTION

A. Authorization

1. Bureau of Ordnance letter to the Naval Research Laboratory, NP 14 (IRe4e) dated 11 February 1944.

B. Statement of Problem

2. The U.S. Naval Technical Mission operating in Europe at the close of the war reported that the Germans had developed a method of reducing reflection from optical surfaces through the use of three superimposed films of different refractive indices.(1) An examination of some samples of these coatings(2) showed them to have very low reflection for practically all wave lengths of the visible spectrum. The object of this investigation was to examine critically this process for reducing reflection and to determine whether or not the American Optical Company type of coatings (used for two-coat reflection-reducing films)(3-5) could be adapted to produce effective three-coat reflection-reducing films.

C. Known Facts Bearing on the Problem

3. Previous work on the subject of reflection-reducing coatings(3-5) done at this Laboratory had given some familiarity with the principles involved in multilayered films. Also, a report of the Naval Technical Mission in Europe(1) and microfilms of several foreign patents(6,7) dealing with the subject of three-layered and multilayered reflection-reducing films were available. According to the report of the Naval Technical Mission,(1) the German coatings were composed of a quarter-wave film (optical thickness) of mixed titanium and silicon dioxides ($n = 1.80$) deposited on the glass, followed by a half-wave film of titanium dioxide ($n = 2.40$), and finally topped by a quarter-wave film of silicon dioxide ($n = 1.45$). These coatings were most satisfactorily applied by use of a vapor-deposition method though some coatings had been applied through use of colloidal solutions of titanium and silicon compounds which revert to the oxides on heating.

II. THEORETICAL CONSIDERATIONS

4. The analysis of the reflection from a three-layered film on a transparent surface involves the evaluation of the sum of the reflections from the four interfaces (glass-film 1, film 1-film 2, film 2-film 3, film 3-air) and must account for interaction (interference) between the various reflections and multiple reflections. This has been simplified by the use of the general theory developed by Dr. B. Salzberg(8) for the evaluation of the reflection of coatings of "n" layers. One form of this theory was applied previously to the analysis of two-coat films.(5)

The equation for the reflection of three-layered films is necessarily more complex, but may be used with no great difficulty when in the following form (which assumes the incident light to be normal to the coated surface):

$$R = \left| \left(\frac{Z_4}{K_o} - 1 \right) \Big/ \left(\frac{Z_4}{K_o} + 1 \right) \right|^2$$

where

$$\frac{Z_4}{K_o} = (n_2 n_3 n_4 - n_2^2 n_4 \tan w_2 \tan w_3 - n_2^2 n_3 \tan w_2 \tan w_4 \ldots$$
$$- n_2 n_3^2 \tan w_3 \tan w_4) + i\,(n_1 n_3 n_4 \tan w_2 + n_1 n_2 n_4 \tan w_3$$
$$+ n_1 n_2 n_3 \tan w_4 - n_1 n_3^2 \tan w_2 \tan w_3 \tan w_4) \;/\; (n_1 n_2 n_3 n_4 \ldots$$
$$- n_1 n_3^2 n_4 \tan w_2 \tan w_3 - n_1 n_3 n_4^2 \tan w_2 \tan w_4 - n_1 n_2 n_4^2 \ldots$$
$$\tan w_3 \tan w_4) + i\,(n_2^2 n_3 n_4 \tan w_2 + n_2 n_3^2 n_4 \tan w_3 \ldots$$
$$+ n_2 n_3 n_4^2 \tan w_4 - n_2^2 n_4^2 \tan w_2 \tan w_3 \tan w_4)$$

and where $w_j = \dfrac{2\ n_j d_j}{\lambda}$

n_1 = index of coated material (glass)

n_2 = index of first (bottom) layer, d_2 its thickness

n_3 = index of second (middle) layer, d_3 its thickness

n_4 = index of third (top) layer, d_4 its thickness

λ = wave length of incident light

$i = (-1)^{\frac{1}{2}}$

III. OUTLINE OF PROCEDURE

5. The method of attack consisted in working out the conditions necessary for the preparation of quarter-wave films having reflection maxima at a given wave length and having the desired refractive indices. This was done by preparing a number of series of glass discs coated with single films of different compositions under various conditions and then determining the desired coating procedures from the positions and values of the reflection maxima. The values of the refractive indices of the films were determined from the values of the maxima of the spectral reflection curves and the index of the glass coated, by use of the following relations:

$$N_f = \left[N_g \, (1 + R^{\frac{1}{2}}) \;/\; (1 - R^{\frac{1}{2}}) \right]^{\frac{1}{2}}$$

In cases where the refractive index of the film is less than that of the material coated, the minimum of the reflection curve is used.

6. Half-wave films (optical thickness) of the desired thickness and index were prepared by superimposing two quarter-wave films of the desired index and gave indication of the feasibility of this method of superposition for producing multilayered films whose final thickness was the sum of the thicknesses of the individual films.

7. All of the sample discs were coated on both sides. The reflection per surface was calculated from the reflection for the pair of surfaces by the relation,

$$R_1 = \frac{R_2}{2 - R_2}$$

where R_1 is the reflection from a single surface and R_2 is the total reflection from the pair of surfaces.

IV. METHODS

A. Apparatus

8. The apparatus for applying the coatings consisted of a centrifuge modified by a special head which would hold a two-inch glass disc and rotate it in a horizontal plane. The speed of rotation was controlled by means of a variable voltage transformer ("Variac") connected to the centrifuge motor and was measured by means of a "Strobotac" mounted above the centrifuge. All coating was done in a room of low humidity (10-20% relative humidity).

9. Spectral transmission curves were obtained by use of a Beckman Quartz Spectrophotometer. Reflections were calculated from transmissions assuming no absorption losses. A number of spectral reflection and transmission curves were determined at the Naval Gun Factory through use of a General Electric Recording Spectrophotometer.

B. Materials

10. (a) Glass discs, 2" diameter x 1/8" thick, about 1.528 index from Semon-Bache & Company, New York.

(b) Solution #155(a). Titanium tetrachloride in ethyl alcohol (see appendix).

(c) Solutions #158-C, #158-D, #158-F. Titanium tetrachloride and ethyl orthosilicate in a solvent essentially ethyl alcohol (see appendix).

(d) Solution #50-Z. Ethyl orthosilicate in a suitable solvent (see appendix).

(e) Titanium tetrachloride, C.P., from Eimer and Amend, New York.

(f) Tetraethyl orthosilicate, ("passed"), from Carbide and Carbon Chemicals Corporation, New York.

C. Preparation of Films

11. The disc to be coated was mounted in the chuck of the centrifuge, spun at the desired rate, and a few drops of the coating solution applied to the center of the disc with a dropper. The solution was applied in one operation - no evaporation was permitted to take place until all of the solution had been added. The disc was spun for 20-30 seconds to dry the coating, allowed to stand 15-30 minutes and then heated at 50-60°C for ten minutes in the room of low humidity. It was finally baked at 400°C for one hour to harden the coating. For the multilayered films the above process was repeated using the appropriate solutions and rates of rotation until the desired number of layers had been applied.

12. Quarter-wave films (a quarter-wave in optical thickness for light of 5250 A° wave length) of medium index (about 1.80) were deposited on the glass discs by applying solution #158-F at 2000 r.p.m. according to the above procedure. The desired conditions were determined from spectral curves of a series of discs coated with the above solution at various rates. Other solutions were tested but were rejected because the index of the resulting coatings was not of the desired value: #158-C produced films having an index of about 1.90 and a maximum at 5000 A° when applied at 1500 r.p.m. and #158-D produced films having an index of about 1.77 and a maximum at 5250 A° when applied at 2500 r.p.m. Solution #158-F evolved from a combination of the above solutions.

13. Quarter-wave films of high index (about 2.09) were deposited on glass discs by applying solution #155(a) at 1500 r.p.m. according to the above technique. Half-wave films of this material were produced by the superposition of two quarter-wave films. Examination of the spectral curves of the quarter and half-wave films indicated this procedure to be reliable.

14. To find the best conditions for applying the top layer of the three-layered films, solution #50-Z was applied at various rates to a series of discs already coated with the correct quarter and half-wave films. Examination of the spectral curves of the members of this series indicated which speed was best for the application of the top layer. This rate was found to be about 5000 r.p.m., under which conditions a film of low index (1.47) approximately a quarter-wave length in optical thickness was deposited.

V. RESULTS

15. Examination of the equation for the reflection of three-layered coatings indicated that with the layers respectively a quarter-wave, a half-wave and a quarter-wave length in optical thickness zero reflection could be obtained only when the following relation held:

$$n_2 = \left(n_1 n_4^2 \right)^{\frac{1}{2}}$$

This expression is independent of the refractive index of the half-wave film. Thus, by having $n_1 = 1.53$, $n_2 = 1.80$ and $n_4 = 1.47$, values which are obtainable experimentally, we have a combination that will give essentially zero reflection for some wave length regardless of the index (n_3) of the half-wave thick material. However, the index of the half-wave thick material will have a marked effect on the spectral reflection curve obtained as is shown in Plate I. These calculations indicate that the high index (half-wave) film must have a refractive index of about 2.40 for maximum effectiveness; that is, to give low reflection over the entire visible range.

16. In Plate II is shown the spectral curve obtained with a film a quarter-wave length in optical thickness and having an index of 1.80. For comparison, the theoretical reflection curve of such a coating is included.

17. Plate III shows the spectral reflection curves of a quarter-wave and half-wave films (from two quarter-wave films) of the high index material and indicates that a half-wave film may be prepared by superposition of two quarter-wave films. The index of this material is only 2.09, the highest value that could be obtained using the outlined procedure. Films of higher index have been prepared from this same solution by heating the coatings to 500°C, but it is felt that 400°C is the practical limit for such treatment.

18. The theoretical and experimental reflection curves for coatings composed of a quarter-wave film of 1.80 index and a half-wave film of 2.09 index on glass are shown in Plate IV. This is one of the combinations involved in the three-coat reflection-reducing films. The lack of coincidence of the two curves is probably due to the failure of the thicknesses of the films to be properly matched and to variations of the refractive indices with the wave length of the incident light.

19. The theoretical and experimental reflection curves of a typical three-layered reflection-reducing film are shown in Plate V. This coating was prepared from superimposed films applied to glass ($n = 1.53$) in the following order: (a) a quarter-wave length film of 1.80 index, (b) a half-wave length film of 2.09 index, (c) a quarter-wave length film of 1.47 index. For each film the wave length con-

sidered as a standard was 5250 A°. Here also the divergence of the theoretical and experimental reflection curves may be due to variations in the refractive indices of the materials for different wave lengths or to the failure of the thicknesses of the layers to be properly matched. Whatever the causes, some flattening of the reflection curve has taken place, resulting in lower reflection than was to be expected.

20. The transmission of a glass disc coated on both sides with a three-layered reflection-reducing film is compared with that of a similar uncoated glass disc (Plate VI) and the curves clearly show the large increase in transmission resulting from such a treatment. The transmission, however, is not as great as an examination of the reflection curve (Plate V) would lead one to expect it to be. This divergence is due partly to the absorption of light on passage through the glass disc but primarily to a slight haze that developed in the coating during its preparation. Properly prepared coatings should not have this scattering loss and thus should give even better transmission.

21. Plate VII shows a comparison of the reflection curves of the German three-layered reflection-reducing coating and its component parts[2] and Plate VIII shows the corresponding NRL coatings. Analysis of the German coating indicates the first coating to have a refractive index of about 1.70 and the second to have an index of about 2.40. The top coating presumably has a refractive index of about 1.45. This combination of coatings does not fit the information received as to their usual method of production but the reflection-reducing coating is extremely efficient. Apparently with such a combination of three films it is not necessary to keep either the thicknesses or the indices of the first two layers within narrow limits, provided, of course, that the proper thickness of the low index top coating is applied. Slight deviations in thickness from perfectly matched quarter and half-wave thick films seem to actually broaden the band of low reflection in both the German and NRL coatings.

22. Plate IX shows the reflection curve of a German three-layered reflection-reducing coating[2] prepared by Schott and Genossen (Jena) from colloidal solutions of silicon and titanium compounds and applied through a centrifuge process similar to that described in this report. This coating was of about the same effectiveness in reducing daylight reflection as the NRL coating but was more effective in reducing the reflection in the blue end of the spectrum. However, its abrasion resistance was much lower than that of the NRL coating (Table II).

23. On Plate X are compared the spectral reflection curves of typical coatings of magnesium fluoride, of the two-layered,[5] and of the three-layered type on glass. The luminous reflection of these coatings toward I.C.I. Illuminant C is shown in Table I, where the results are given in terms of the response of the daylight and night

adapted eye. The effectiveness of the three-layered coating produced here approaches that of the three-layered coating produced by Schott and Genossen through vapor deposition and is better than that of the Schott and Genossen solution type coating. All of the three-layered coatings are considerably better than the best of the two-layered type both to the daylight and night adapted eye, and these are, in turn much more effective than the best of the magnesium fluoride evaporated coatings.

24. The results of abrasion tests on some of these coatings are listed in Table II. The three-layered coatings werd not as resistant to abrasion as were two-layered coatings prepared under the same conditions. However, they were durable enough to withstand normal handling and cleaning (rubbing with a handkerchief, etc.). These coatings were much more durable than similar German coatings produced from colloidal solutions but were not as durable as those produced by the vapor-deposition method.[2]

VI. CONCLUSIONS AND RECOMMENDATIONS

25. Very effective reflection-reducing coatings of the three-layered type have been prepared from solutions of the type developed by the American Optical Co. The reduction of reflection was greater than an examination of the theoretical equation would lead one to expect, probably partly due to experimental errors in producing the films and partly to the variation of the refractive indices of the materials for light of different wave lengths. However, the maximum effectiveness to be expected with this type coating cannot be obtained with these materials as none of them has a refractive index as high ($n = 2.40$) as would be required for best results.

26. The recommended procedure for production of three-layered reflection-reducing coatings using the American Optical Company type materials is as follows: (1) Apply solution #158-F to clean glass surfaces at 2000 r.p.m. in a room of low humidity, allow to dry 15 minutes, then bake 10 minutes at 50-60°C before removing from dry room, and finally bake at 400°C for one hour; (2) Apply solution #155(a) at 1500 r.p.m. and treat as above; (3) Re-apply solution #155(a) at 1500 r.p.m. and treat as above; (4) Apply solution #50-Z at 5000 r.p.m. and treat as above. These intermediate bakings have been found necessary to produce films of the desired clarity. When the individual films were not baked before addition of the next coatings, some scattering of light was noted, even though the actual reflection was extremely small.

27. It is recommended that these coatings be used only where the absolute minimum of reflection is desired. The difficulty of producing coatings of this type prohibits their use on the simpler optical instruments.

28. It is recommended that other methods of producing these three-layered coatings be studied. It is suggested that the evaporation technique may be adapted to the production of these coatings, thus making use of equipment already on hand. Unless directed to the contrary, this work will be continued.

VII SUMMARY

1. A study has been made of the adaptation of solutions of the American Optical Co. type to the production of three-layered reflection-reducing coatings and has demonstrated that coatings of the same order of effectiveness as the German coatings may be produced.

2. The most effective three-layered films cannot be prepared using the American Optical Co. type solutions since the material of highest refractive index has a value of only 2.09 rather than about 2.40. Materials of this higher index are available, however, through an evaporation process or through a vapor-deposition process such as that developed by Schott and Genossen, Jena.

3. These three-layered coatings are considerably more difficult to produce than coatings having fewer layers and therefore are practical only for special uses where the ultimate in the reduction of reflection is required.

4. The study of other methods of production of these coatings should be undertaken by those acquainted with other techniques, such as evaporation.

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2. Examination of Samples of Reflection-Reducing Films Produced in Germany. NRL letter S19(5)(455-LBL) 455-7/46 of 23 January 1946.

3. Reflection-Reducing Coatings for Optical Surfaces. NRL Report No. P-2257 of 30 March 1944 (Confidential).

4. Coatings of Low and High Reflectivity for Optical Surfaces. NRL Report No. P-2371 of September, 1944 (Confidential).

5. Survey of Two-Coat Reflection-Reducing Films. NRL Report No. P-2440 of 15 January 1945 (Confidential).

6. Coating to Reduce Surface Reflection. Swiss Patent No. 223,344 of 4 January 1943, issued to Jena Glass Works, Schott and Gen., Jena, Germany.

7. Layer for Altering Reflecting Power from Multiple Superimposed Alternating Films of Two Materials Having Different Refractive Indices. German Patent No. 742,463 of 18 January 1944, issued to Dr. Walter Geffcken, Jena Glass Works, Schott and Gen., Jena, Germany.

8. Private Communication from Dr. B. Salzberg, Consultant, NRL.

APPENDIX

Stock Titanium Solution. Prepared by the slow, careful addition of 15 ml. of titanium tetrachloride to 320 ml. of 95% ethyl alcohol.

Solution #155(a). Prepared by mixing two volumes of the Stock Titanium Solution with one volume of 95% ethyl alcohol.

Solution #158-C. Prepared by mixing 64 ml. of the Stock Titanium Solution with 80 ml. of a solution composed of 51.6 ml. 95% ethyl alcohol, 46.9 ml. ethyl acetate, 5.02 ml. ethyl orthosilicate and 4.0 ml. hydrochloric acid. Allowed to stand overnight.

Solution 158-D. Prepared by mixing 64 ml. of the Stock Titanium Solution with 80 ml. of a solution composed of 52 ml. 95% ethyl alcohol, 47 ml. ethyl acetate, 10 ml. ethyl orthosilicate and 4 ml. hydrochloric acid. Allowed to stand overnight.

Solution #158-F. Prepared by mixing one volume of #158-C with two volumes of #158-D.

Solution #50-Z. Freshly prepared every day by adding 4.0 ml. of ethyl orthosilicate to 25.0 ml. of a stock solvent and allowing to stand thirty minutes. The stock solvent is composed of 440 ml. ethyl alcohol (95%), 400 ml. ethyl acetate, 50 ml. butyl alcohol, and 34 ml. hydrochloric acid.

TABLE I

Luminous Reflection of Coated Discs Toward
I.C.I. Illuminant C.

Coating	Type	Producer	Reflection Daylight	Reflection Night
3-layer	Vapor-deposition	Schott & Gen.	0.21%	0.35%
3-layer	Solution	Schott & Gen.	0.56	0.37
3-layer	Solution	N.R.L.	0.26	0.38
2-layer	Solution	N.R.L.	0.81	0.50
MgF_2	Evaporation	N.G.F.	1.43	1.31

TABLE II

Results of Abrasion Tests

Type of Coating	Producer	Bake	Rubs*	Condition of Coating
3-layered	N.R.L.	400°C	300	Scratched (about 1/20 removed)
3-layered	N.R.L.	400°C	300	Few fine scratches
2-layered	N.R.L.	400°C	300	Unmarked
2-layered	N.R.L.	105°C	300	Removed
Magnesium fluoride	Naval Gun Factory	--	300	Unmarked
3-layered (vapor-deposition)	Schott and Gen. (Jena)	--	300	Very slightly scratched
3-layered (colloidal solution type)	Schott and Gen. (Jena)	--	150	Removed

*Powdered magnesium fluoride used as abrasive in abrader developed at the Naval Gun Factory.

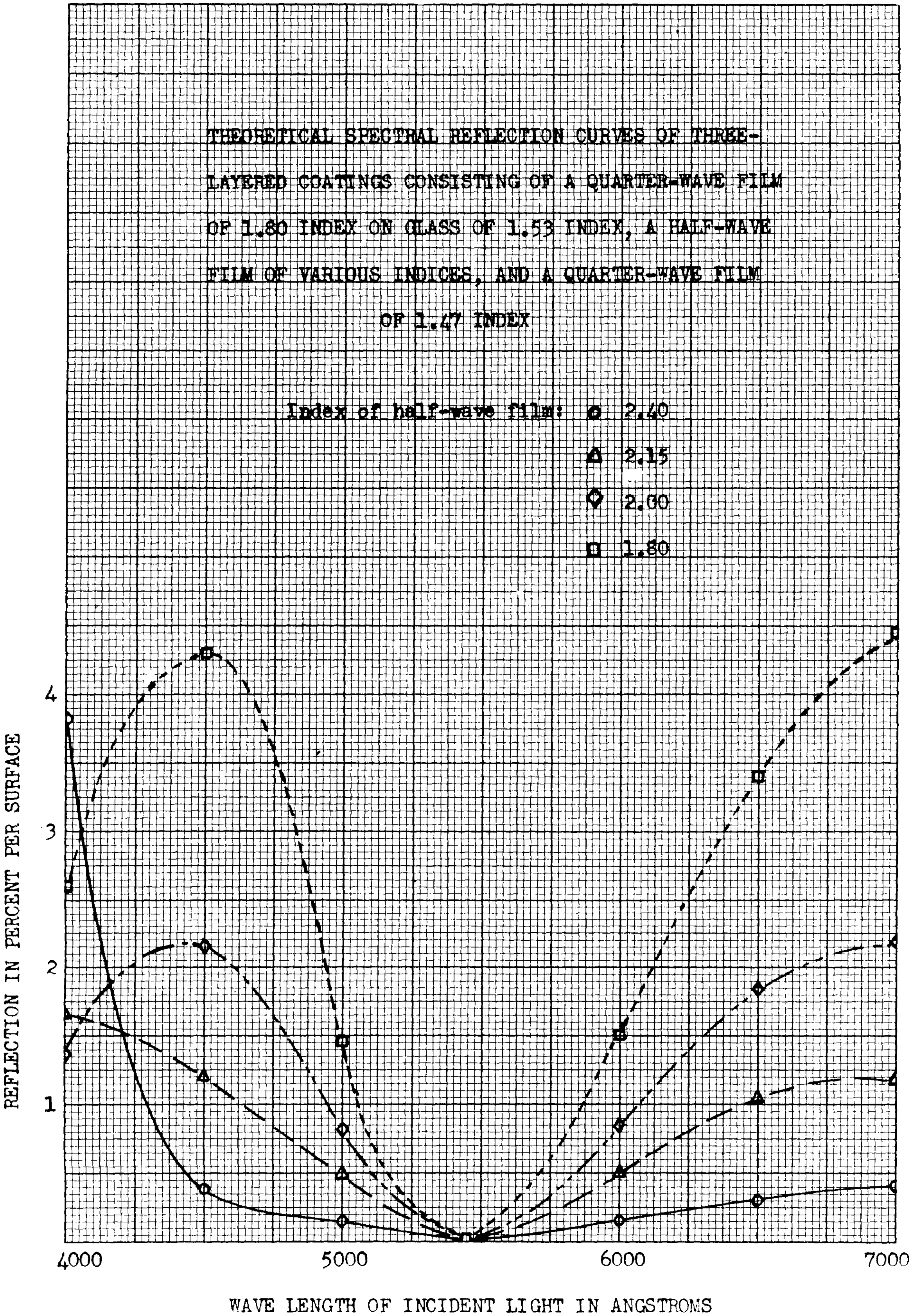

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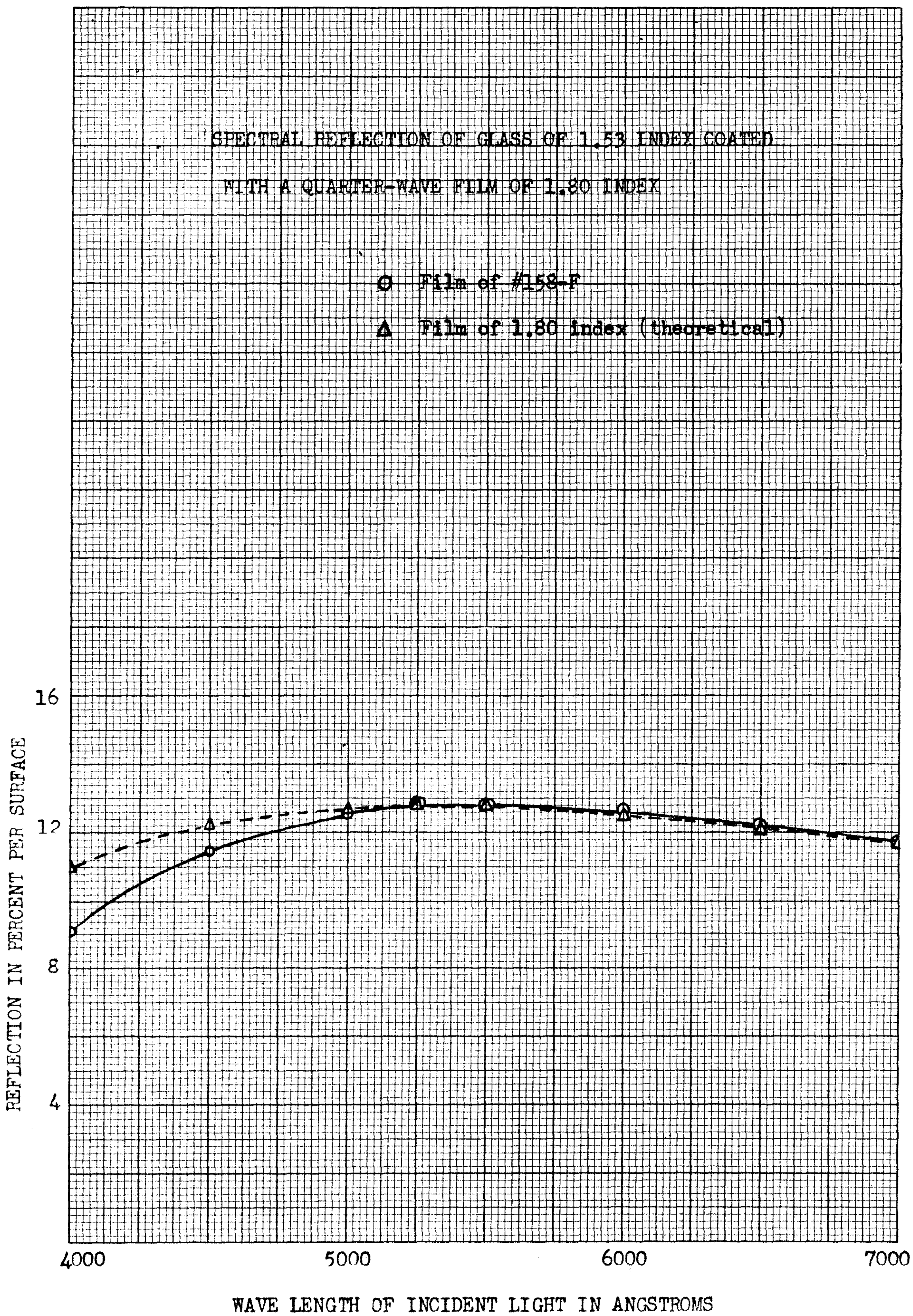
PLATE 1



P-2849 PLATE 2

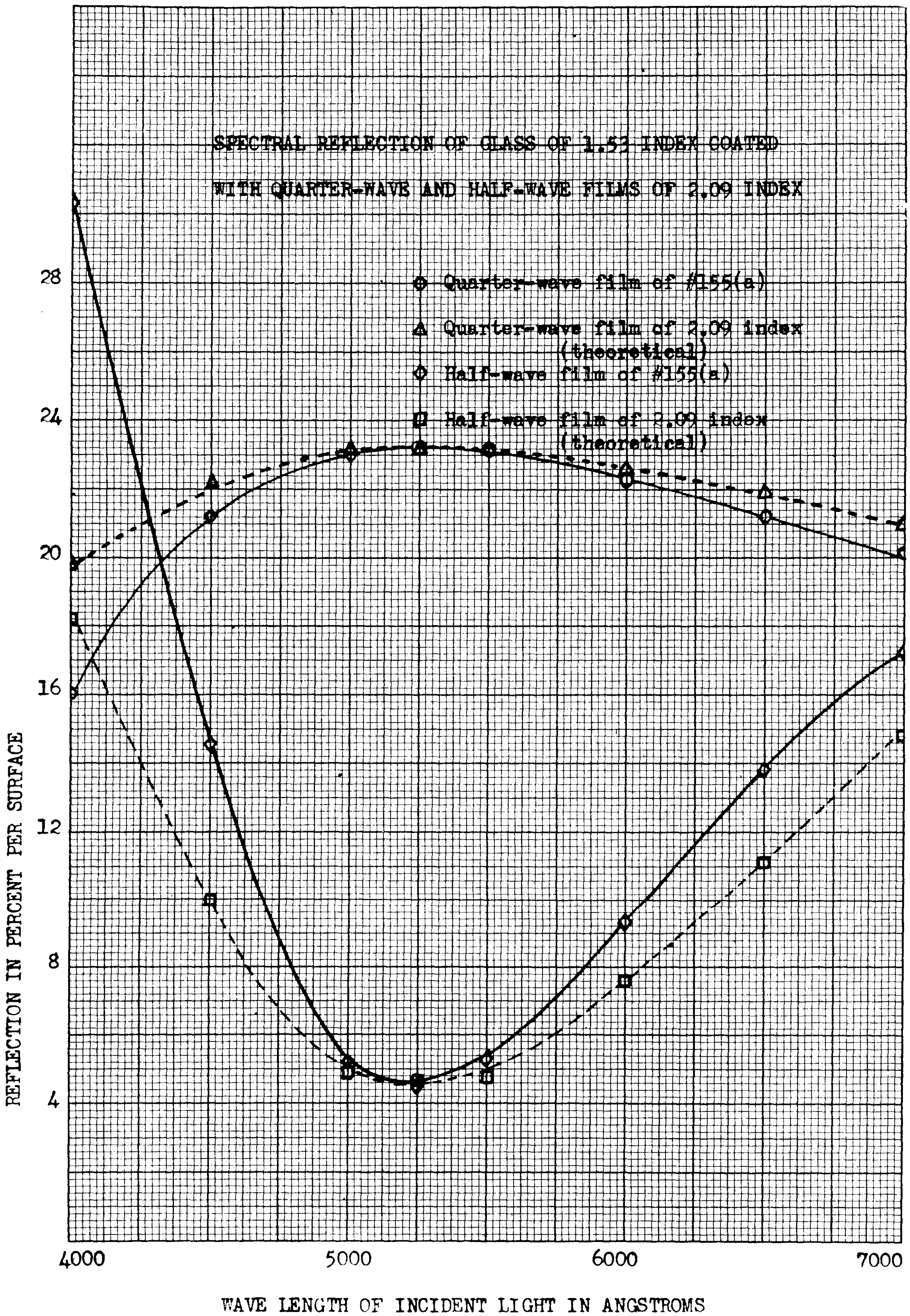


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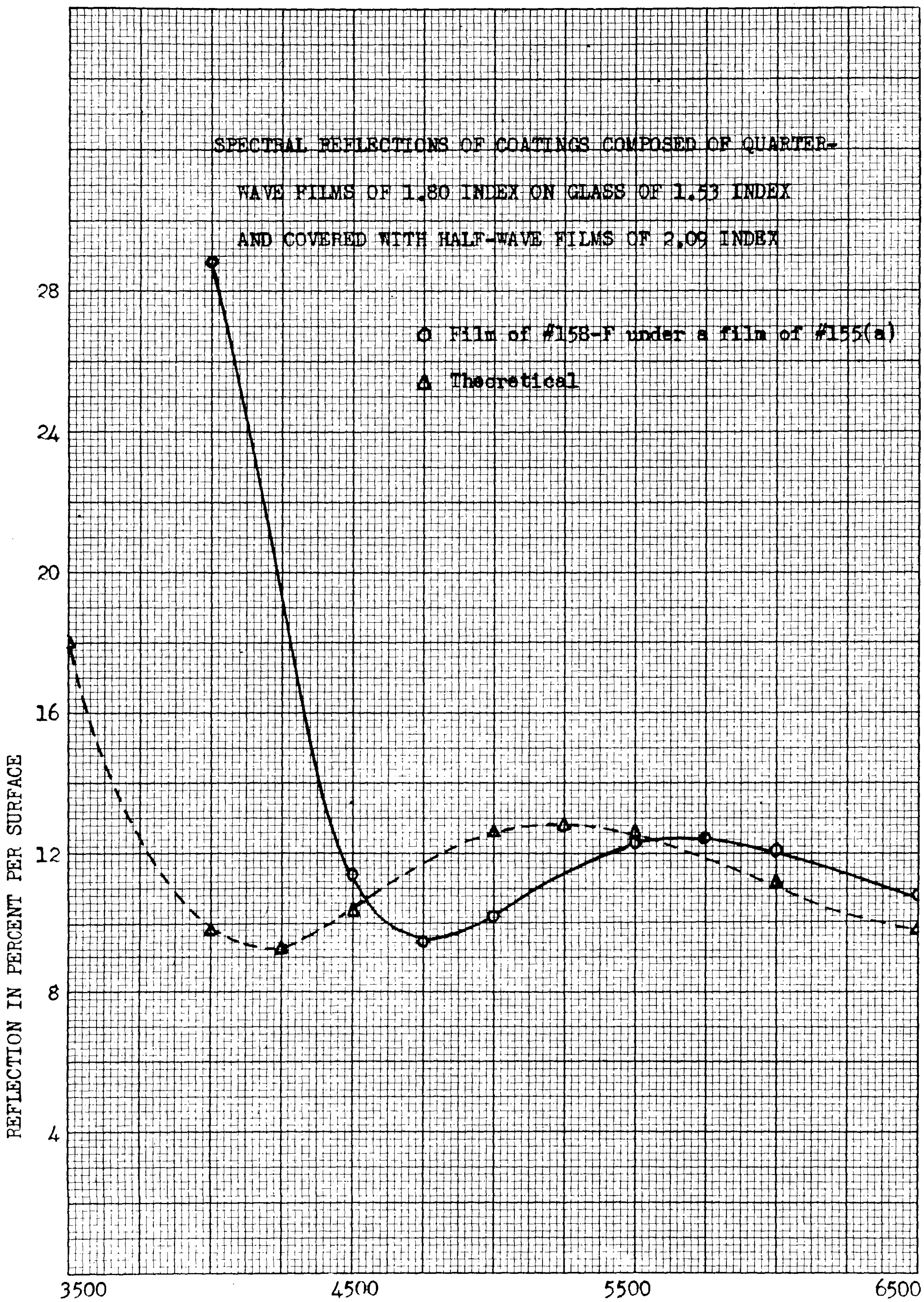
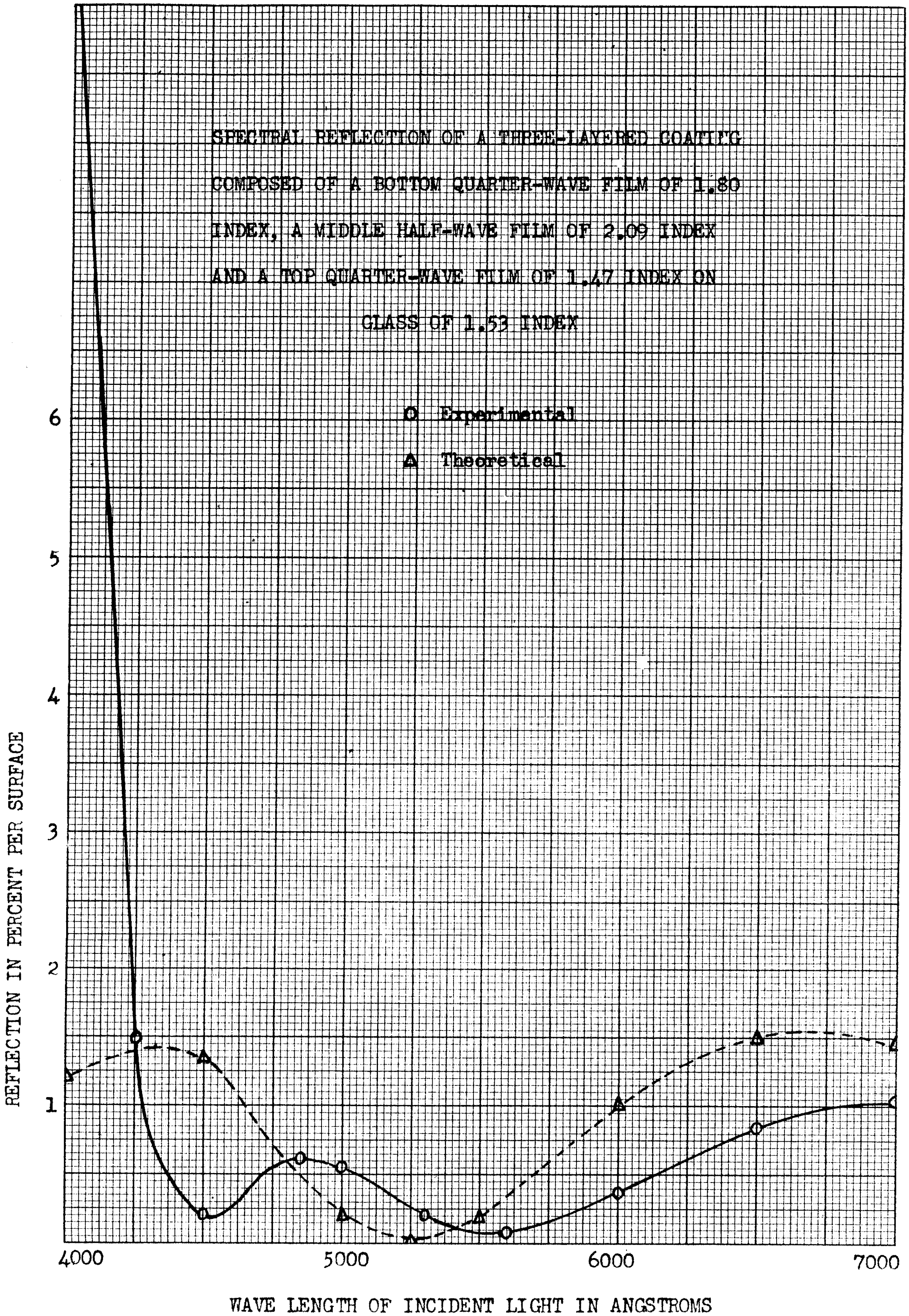
PLATE 3



WAVE LENGTH OF INCIDENT LIGHT IN ANGSTROMS

P-2849 PLATE 4


SPECTRAL REFLECTION OF A THREE-LAYERED COATING
COMPOSED OF A BOTTOM QUARTER-WAVE FILM OF 1.80
INDEX, A MIDDLE HALF-WAVE FILM OF 2.09 INDEX
AND A TOP QUARTER-WAVE FILM OF 1.47 INDEX ON
GLASS OF 1.53 INDEX
O Experimental
Δ Theoretical
REFLECTION IN PERCENT PER SURFACE
6
5
4
3
2
1
4000
5000
6000
7000
WAVE LENGTH OF INCIDENT LIGHT IN ANGSTROMS

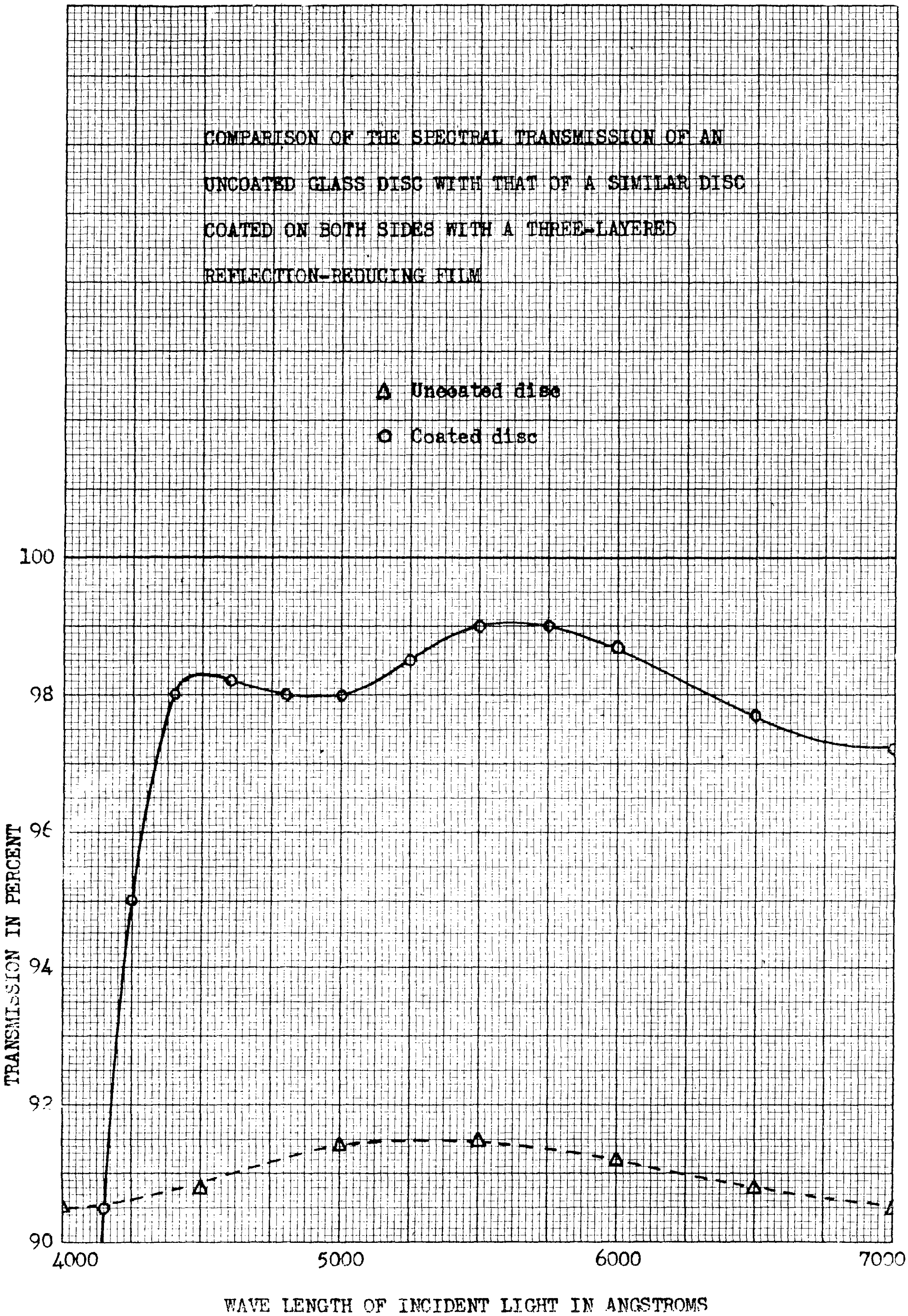


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PLATE 6

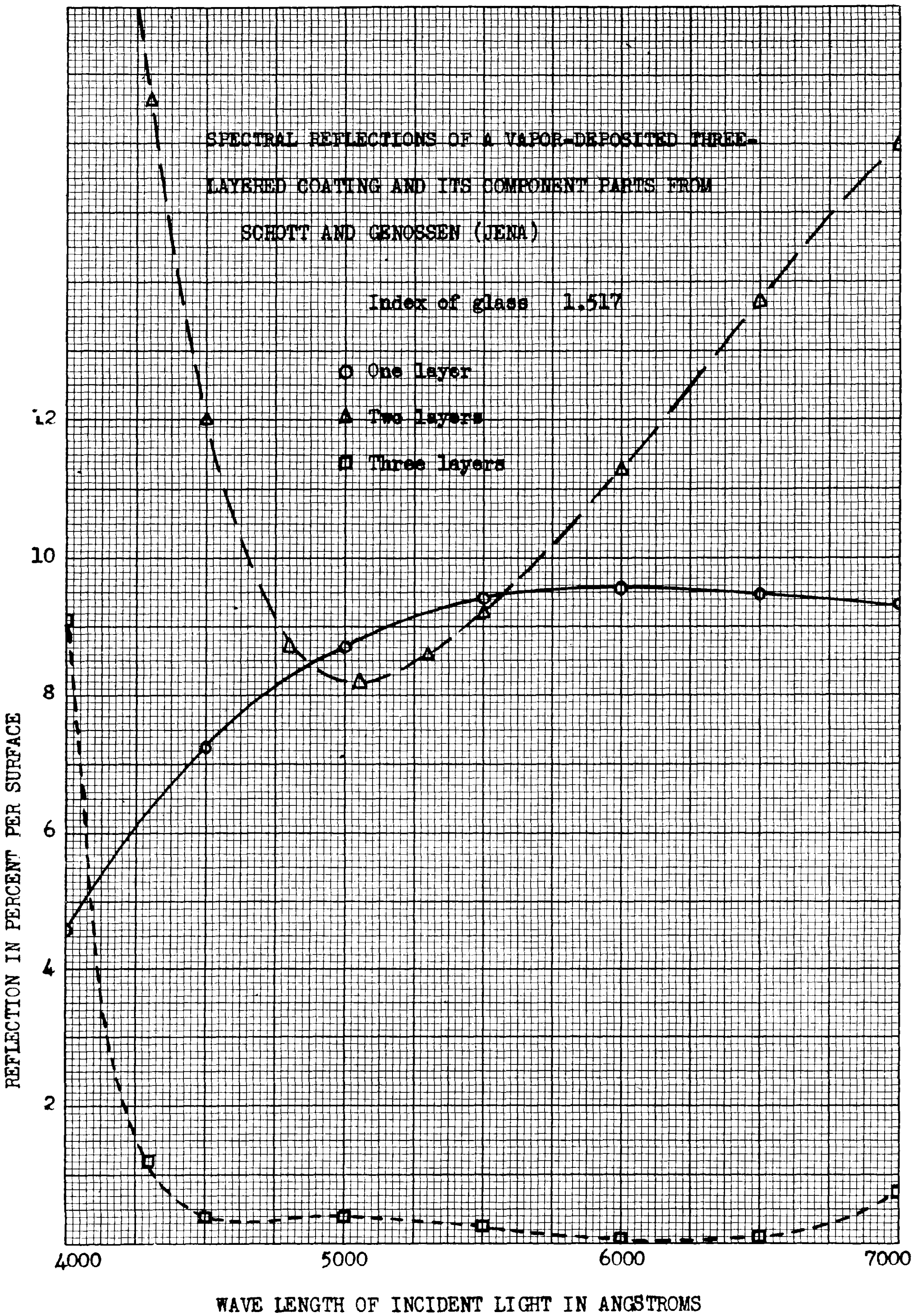

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PLATE 7

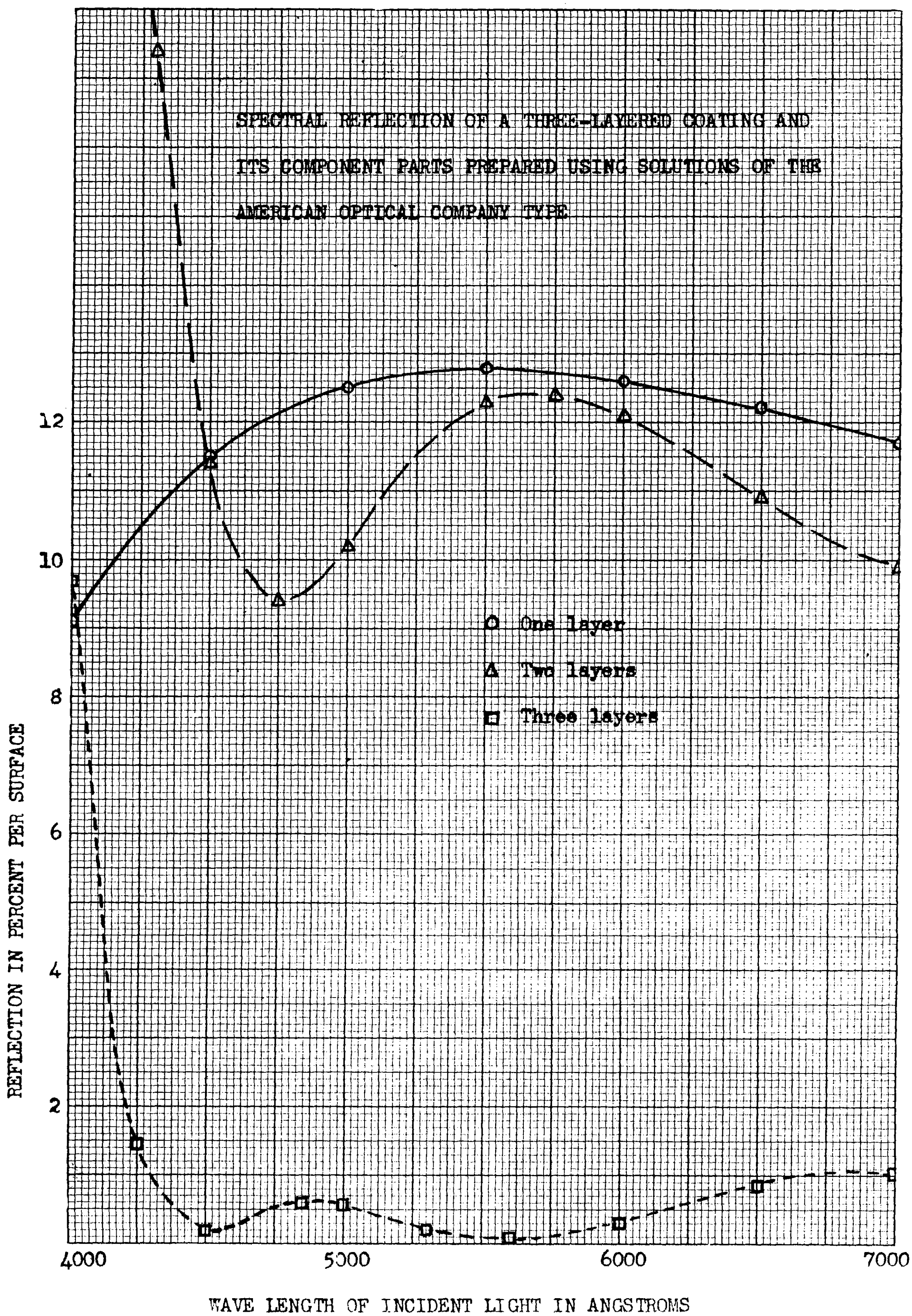

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PLATE 8

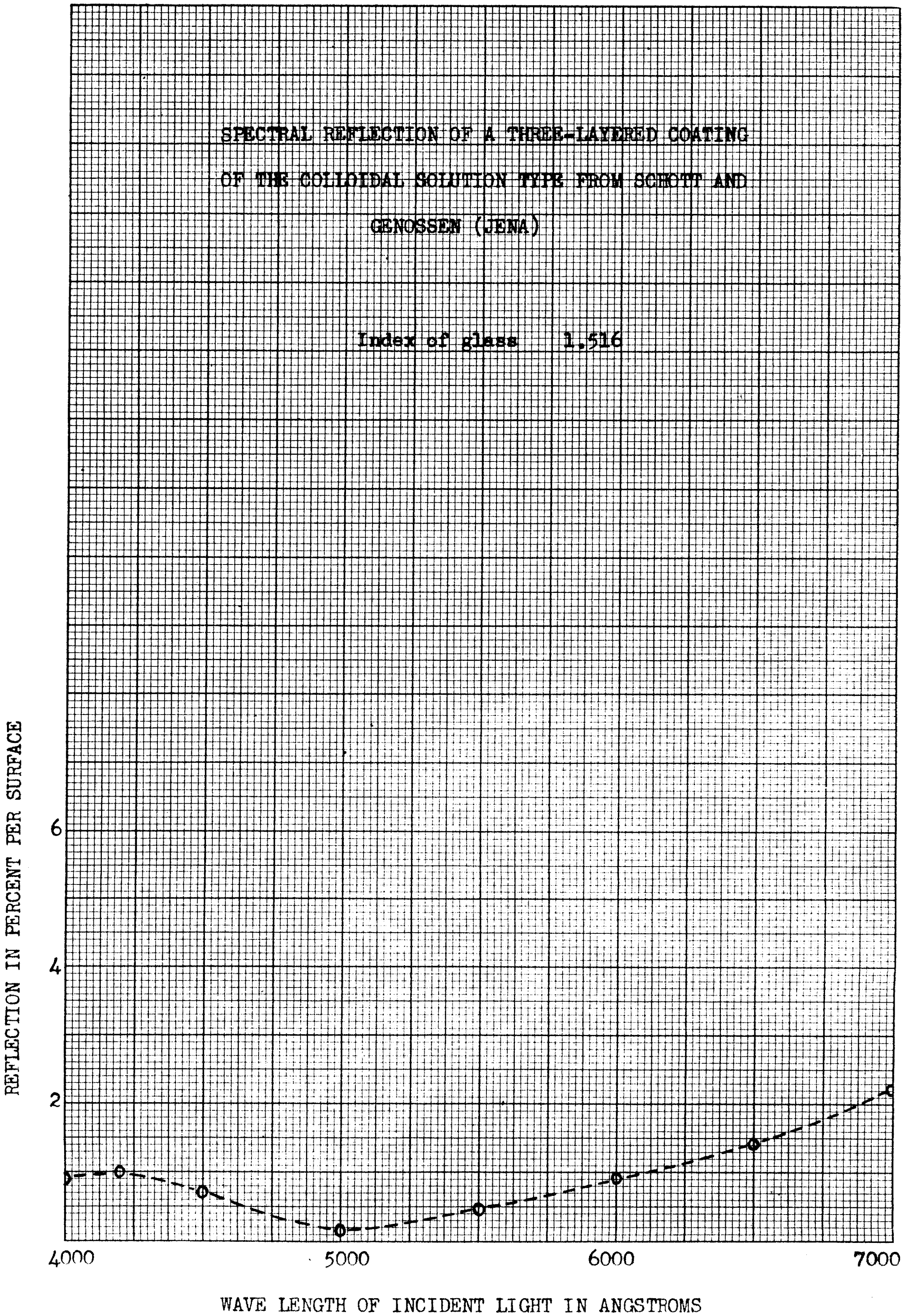

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PLATE 9

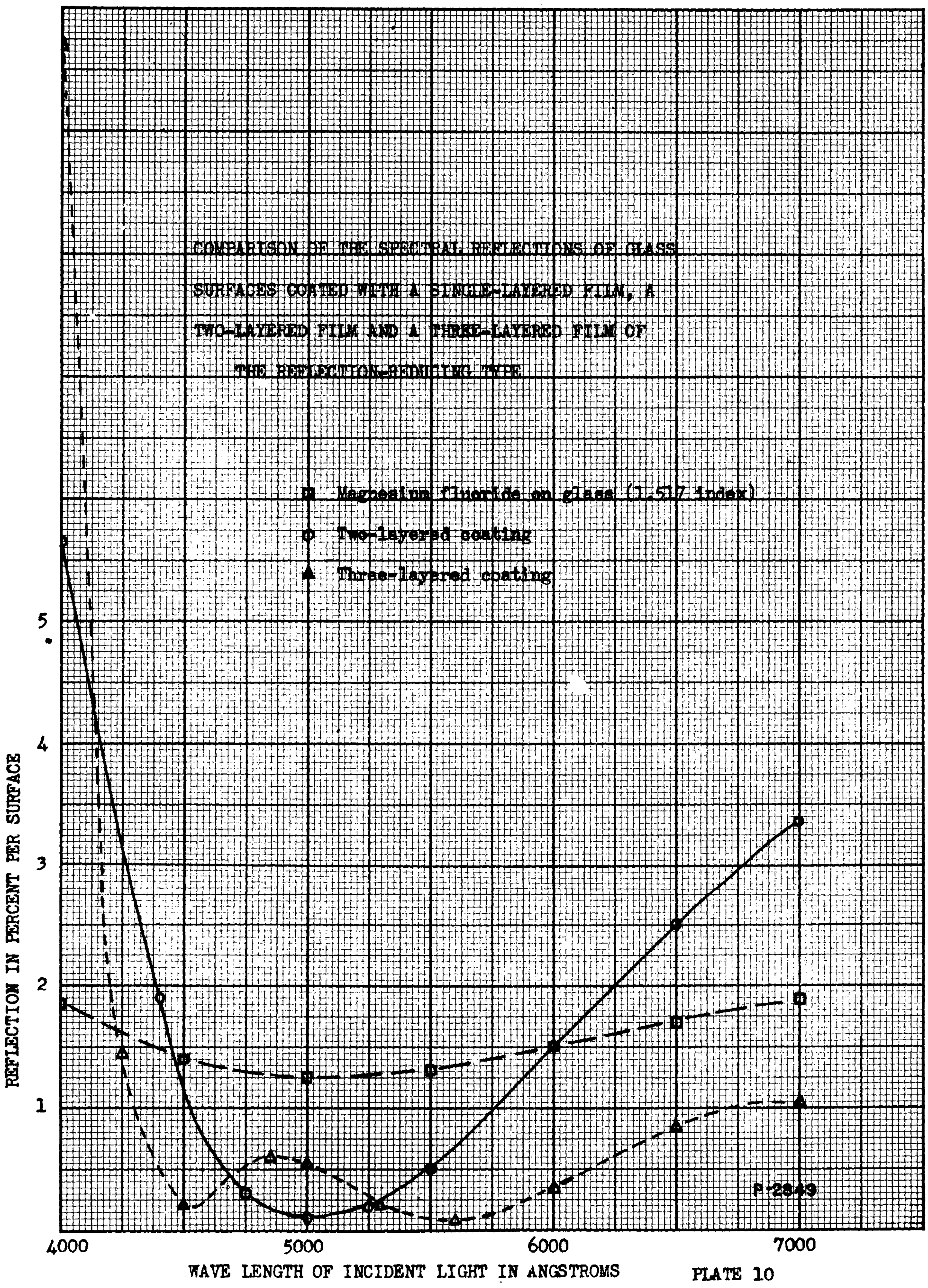
COMPARISON OF THE SPECTRAL REFLECTIONS OF GLASS SURFACES COATED WITH A SINGLE-LAYERED FILM, A TWO-LAYERED FILM AND A THREE-LAYERED FILM OF THE REFLECTION-REDUCING TYPE
Magnesium fluoride on glass (1.517 index)
Two-layered coating
Three-layered coating
REFLECTION IN PERCENT PER SURFACE
1
2
3
4
5
4000
5000
6000
7000
WAVE LENGTH OF INCIDENT LIGHT IN ANGSTROMS
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PLATE 10