Date: 28 February 1944　　　　NRL Report No. H-2246

NAVY DEPARTMENT

Report on

GEIGER COUNTER TECHNIQUE FOR X-RAY DIFFRACTION
PART 2. - A METHOD OF DETERMINING THICKNESSES OF THIN COATINGS

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Number of pages:	Text - 5　　Plates - 3
Authorization:	BuShips Project No. 1129/42

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Distribution: BuShips (5)

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I. A METHOD OF DETERMINING THICKNESSES OF THIN COATINGS

Thickness determination by measurement of X-ray transmission is based on the exponential absorption law

$$\frac{I_x}{I_o} = e^{-\mu p x} \qquad (1)$$

For most materials, the mass absorption coefficient, μ , and the density, ρ , are known or readily measured. The ratio of transmitted to incident intensity, I_x/I_o, is generally measured with a Geiger counter or ionization chamber. Measurements of this type are treated in NRL Report M-1799, where it is shown that reliable results are obtainable for thicknesses varying from hundred thousandths of an inch, using soft X-rays, to as high as several inches with high voltage radiation. The present report describes a method of adapting X-ray transmission for measuring thin coating or plating thicknesses from one side. The method described below has certain desirable features not obtainable in most standard practices, (Appendix II). It is essentially non-destructive; it measures non-metallic or metallic coatings on either type of backing; it determines separate thicknesses in multi-layer coatings of different substances; it measures mass per unit area independently of backing surface or front surface roughness; a single measurement may be an average over a surface area as large as one square inch or as small as one-quarter square millimeter; external surfaces of almost any shape may be handled; when supplemented by electron microscope information, the thickness of coatings on small particles in the pigment range can be estimated.

To measure X-ray transmission from one side, the beam must be reflected from the backing material. Every crystalline substance reflects monochromatic X-rays coherently at specific angles given by the Bragg diffraction formula,

$$n\lambda = 2\, d \sin\theta \quad , \qquad (2)$$

where λ is the X-ray wavelength, d is the crystalline spacing giving rise to a reflection at the angle θ, and n is the order of diffraction. Each substance has a unique set of planar spacings d_{hkl}, and associated reflection angles, θ_{hkl}. As an illustration of the procedure for measurement of an electroplated coating consider the example of copper plating on a silver backing. Copper characteristic radiation is reflected most strongly from silver at an angle of 38.1 degrees. A second strong reflection occurs at 77.6 degrees. MoKα rays are reflected strongly at 17.3 degrees and FeKα rays at 48.4 degrees. Referring to Plate (1), if I_o is the intensity reflected from the unplated silver, and I_1, that from the copper plated silver (see Appendix I), the ratio I_1/I_o is given by

$$\frac{I_1}{I_o} = e^{-\mu_{cu} \cdot \rho_{cu} \cdot \frac{2X_{cu}}{\sin\theta}} \qquad (3)$$

Plate 2 shows the variation of I_1/I_o with thickness of the copper plating, and with hardness of the X-rays. Plate 3 plots corresponding data for aluminum on silver. The Geiger counter spectrometer described in NRL Report H-2235 serves conveniently for laboratory measurements of this type.

When a given intensity is measured repeatedly with a Geiger counter, the individual results show a statistical distribution about the true value. The probable error in any set of counts, N, is given by

$$P.E. = 0.67\, N^{\frac{1}{2}} \qquad (4)$$

The relative probable error is

$$\frac{P.E.}{N} = \frac{0.67\sqrt{N}}{N} = \frac{0.67}{\sqrt{N}} \qquad (5)$$

For a probable error of 1.0 percent, 4500 pulses must be counted. To reduce the probable error to 0.1 percent, the count must be raised to 450,000. When the results of two intensity measurements appear in a ratio, I_1/I_o, the relative probable error of the ratio is computed from

$$\frac{P.E}{N_{I_1}/N_{I_o}} = 0.67\left(\frac{P.E._{I_1}{}^2}{N_{I_1}{}^2} + \frac{P.E_{I_o}{}^2}{N_{I_o}{}^2}\right)^{\frac{1}{2}} = 0.67\left(\frac{1}{N_1} + \frac{1}{N_2}\right)^{\frac{1}{2}} \qquad (6)$$

With the aid of equation (6) it is possible to estimate the accuracy of any measurement of plating thickness by the method described above. If all instrumental errors are eliminated, any desired accuracy is theoretically obtainable by counting over a sufficiently long period. From Plate 2, the ratio $\frac{I_1}{I_o}$ is .94 for 10^{-5} cms. of copper if MoKα radiation is used (Curve 1). Assuming a counting rate of 200 counts per second (which is readily obtainable with the instrument described in H-2035), equation (6) shows that counting I_1 and I_o for one minute each will determine a thickness of 10^{-5} cms within probable error limits of ± 0.1 x 10^{-5} cms. At the other end of the scale, (Curve 3), if CuK radiation is employed a thickness of 10^{-3} cms may be determined within ± .04 x 10^{-3} cms by again counting one minute for I_1 and for I_o. In every case the probable error may be decreased by longer counting, but only in proportion to the square root of the length of the counting period. The validity of the method has been checked against calculations based on plating conditions and against micrometer measurements on foils.

In applying the technique to non-metallic materials, a two element compound is treated as two superposed monatomic structures. Densities and absorption coefficients are assigned individually to the respective elements. For example, if the compound is A_2B of density, ρ, with atomic weights N_A and N_B, for the component atoms,

$$\frac{\rho_A}{\rho_B} = \frac{2N_A}{N_B} \qquad (7)$$

and

$$\rho_A + \rho_B = \rho \qquad (8)$$

from which ρ_A and ρ_B may be computed. The measured ratio $\frac{I}{I_o}$ is then expressed by

$$\frac{I}{I_o} = \left(e^{-\mu_A \rho_A X}\right)\left(e^{-\mu_B \rho_B X}\right) = e^{-(\mu_A \rho_A + \mu_B \rho_B) X} \qquad (9)$$

where X is the thickness of the compound layer. The extension of the treatment to more than two components follows in similar fashion.

In multilayer coatings, each thickness may be determined by first solving for the upper layer, next for the sum of the first two layers, then the sum of the first three layers, and so on.

If the backing surface is rough, but not so rough as to permit undercutting by the coating one obtains the mass of coating per unit area by solving for ρX.

If the diffraction spectrometer is used, the width of the beam striking the specimen is controlled by the slit system. The focusing properties of the spectrometer permit the covering of an area as large as one square centimeter on a flat surface in a single measurement. The lower limit for practical purposes may be set at about one quarter square millimeter. If large objects must be handled the standard specimen holder may be replaced with any suitable device for holding the test surface in position.

II. APPENDIX I

EFFECT OF GENERAL AND FLUORESCENT SCATTERED RADIATION

It is incorrect to assume that I_1 in equation (3) is made up entirely of $K\alpha$ radiation transmitted through the plating layer. If any material is irradiated with X-rays harder than the minimum required to ionize the K shell, the entire fluorescent X-ray spectrum is excited. Even if the $K\alpha$ radiation of the target employed is softer than the radiation required to excite fluorescence, there is always present in the continuous spectrum X-rays of much shorter wavelength than the $K\alpha$ lines. Fluorescent rays excited by the high energy end of the continuous spectrum and general scattering contribute an appreciable background radiation. The influence of background radiation on measurement of thickness by the method described above may be considerably reduced by the use of suitable filters or almost completely removed by means of a crystal monochromator, but this latter step is unnecessary. The coherent reflection from the silver is limited to an angular range less than one degree in 2θ. A measurement of intensity of the background radiation away from this line, gives the extra intensity due to general and fluorescent scattering. Subtracting this background from the total intensity measured at the Bragg angle leaves only the intensity truly transmitted through the thin layer.

III. APPENDIX II

METHODS OF MEASURING THICKNESS OF PLATINGS

In a recent discussion(1) of the techniques of testing thickness of electrodeposits, the various methods were classified as follows:

(1) Direct Measurement

<u>Micrometer</u> - The method is crude for thicknesses less than one-thousandth of an inch.

<u>Microscope</u> - Measurement is made on a polished cross-section of the plated article.

<u>Chord</u> - Coatings on flat surfaces are just cut through by a circular grinding wheel of radius (R). The width of the cut (the chord) C, is accurately measured and the thickness (T) is computed from

$$T = \frac{C^2}{8R}$$

(2) Time Methods

The time required for a corrosive solution to penetrate a plating is measured. The deposit must be perfectly clean before testing since the slightest film of grease or oxide affects the rate of attack.

Immersion - The specimen is immersed in the reagent and the period required for penetration is timed. The reagent is standardized against deposits of known thickness and the rate of penetration at a range of temperatures plotted on a calibration chart. The method is applied to testing chromium, zinc and cadmium plating.

Jet Test - A fine continuous stream of the reagent is allowed to impinge on the plated surface until the deposit is penetrated. The time is measured. Important precautions are to ensure that there is absolutely no movement of the specimen during test and to take care that spent solution can run away freely from the inspection point. The jet test is not applicable to very small complex surfaces or to points near the edge of large surfaces.

Dropping Tests - Penetrating solution is delivered from a capillary tube in a series of drops. The number of drops per second is controlled at about 100 drops per minute.

(3) Magnetic Measurements

They rely on measuring the difference in magnetic properties of the deposit compared with the base metal, e.g., slightly magnetic deposits such as nickel on non-magnetic deposits, such as brass; or non-magnetic coatings such as zinc, on highly magnetic metals, such as steel. The magnetic conditions vary with thickness of the plating.

Permanent Magnet - The attractive force of a permanent magnet is measured by a steel spring and recorded on a dial.

Electro-Magnetic Type - This type measures the variation in flux of a magnetic circuit, created by the electro deposited coating.

(4) Weighing Methods

These methods essentially consist of a determination of the total weight of a deposit on a known area.

(1) Reference: The Metal Industry - Vol. 63, No. 6, Aug. 6, 1943, page 90.

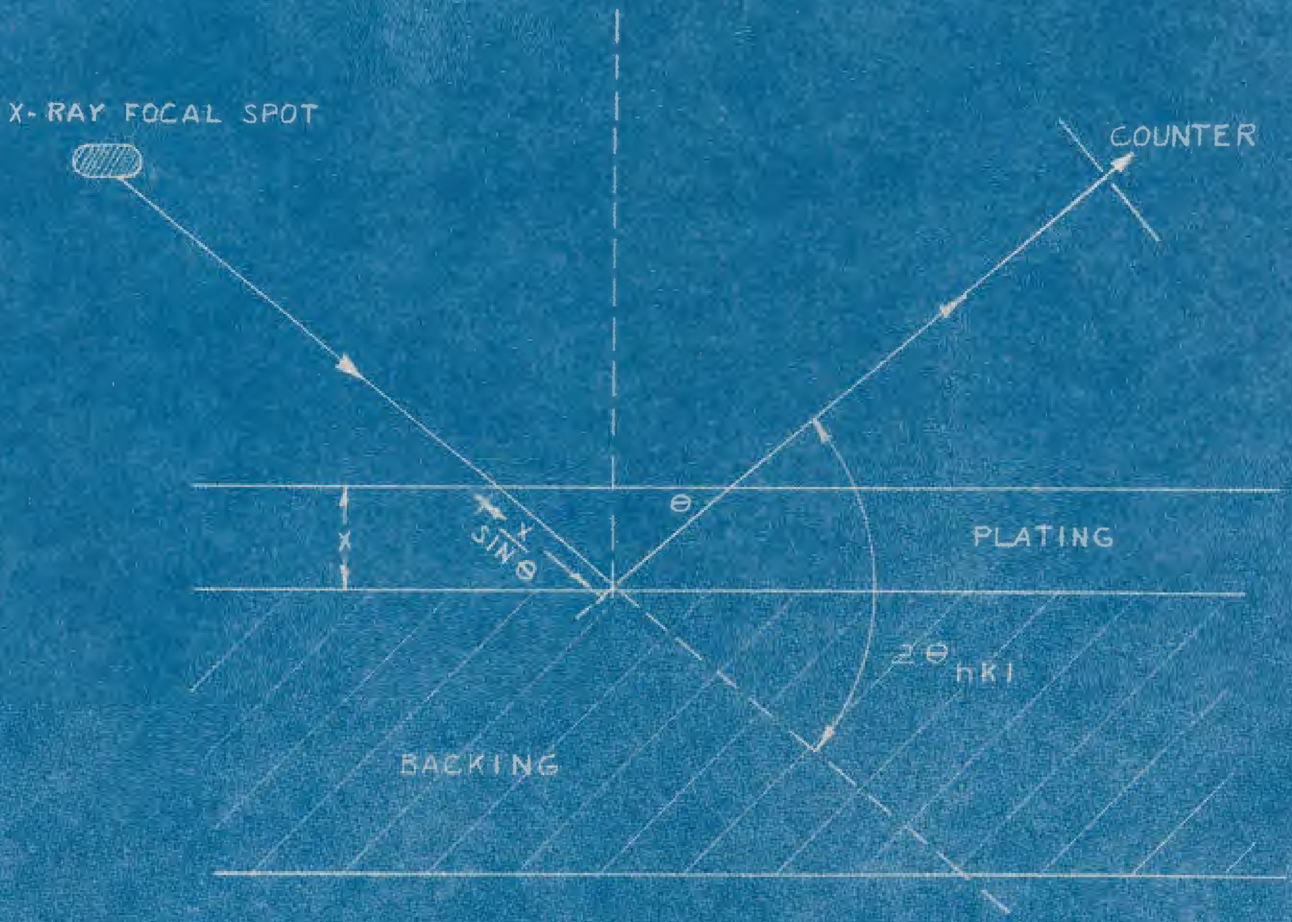

PLATE I

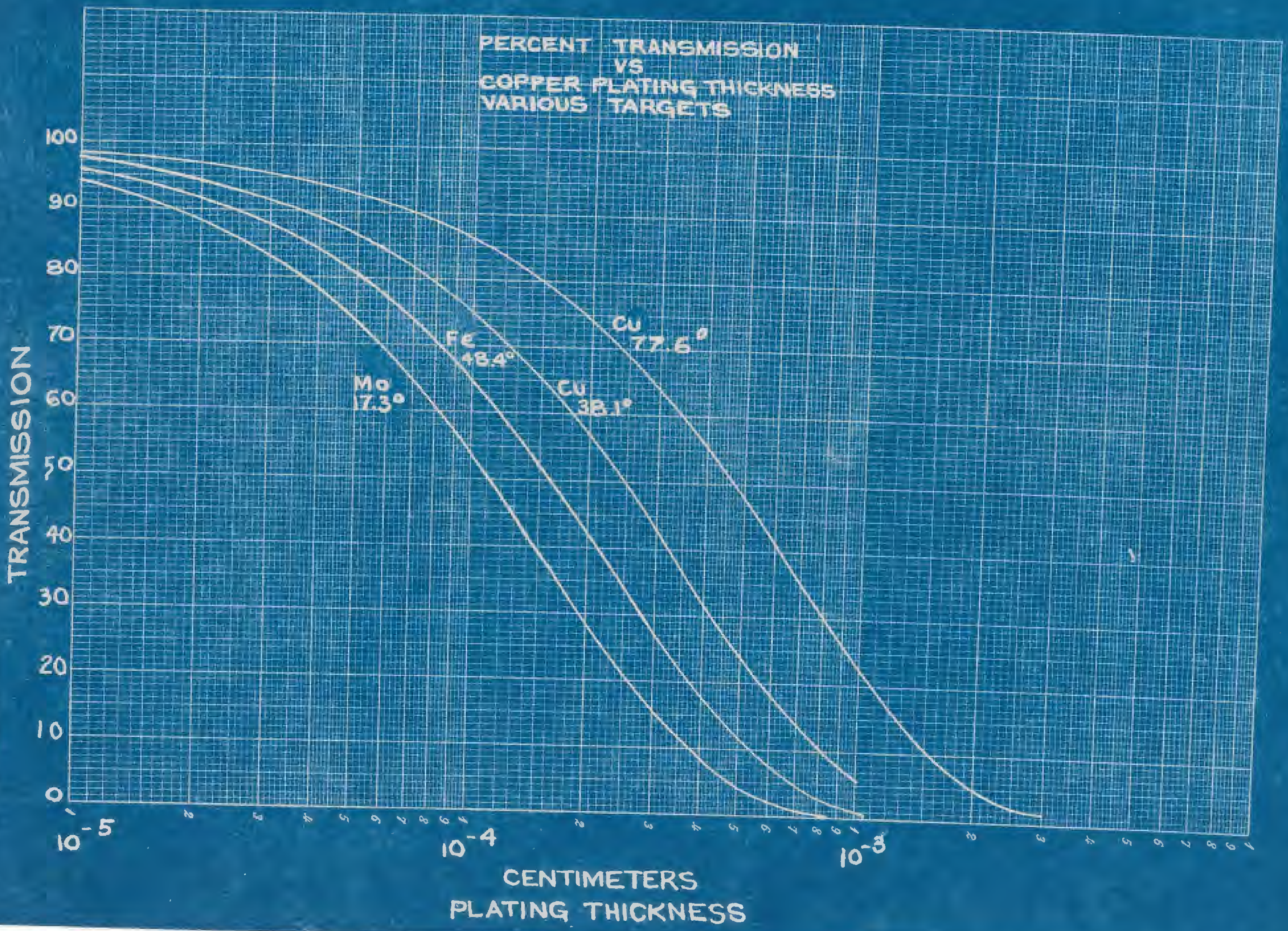
PERCENT TRANSMISSION
VS
COPPER PLATING THICKNESS
VARIOUS TARGETS
Cu 77.6°
Fe 48.4°
Cu 38.1°
Mo 17.3°
TRANSMISSION
100
90
80
70
60
50
40
30
20
10
0
10-5
10-4
10-3
CENTIMETERS
PLATING THICKNESS

PLATE 2

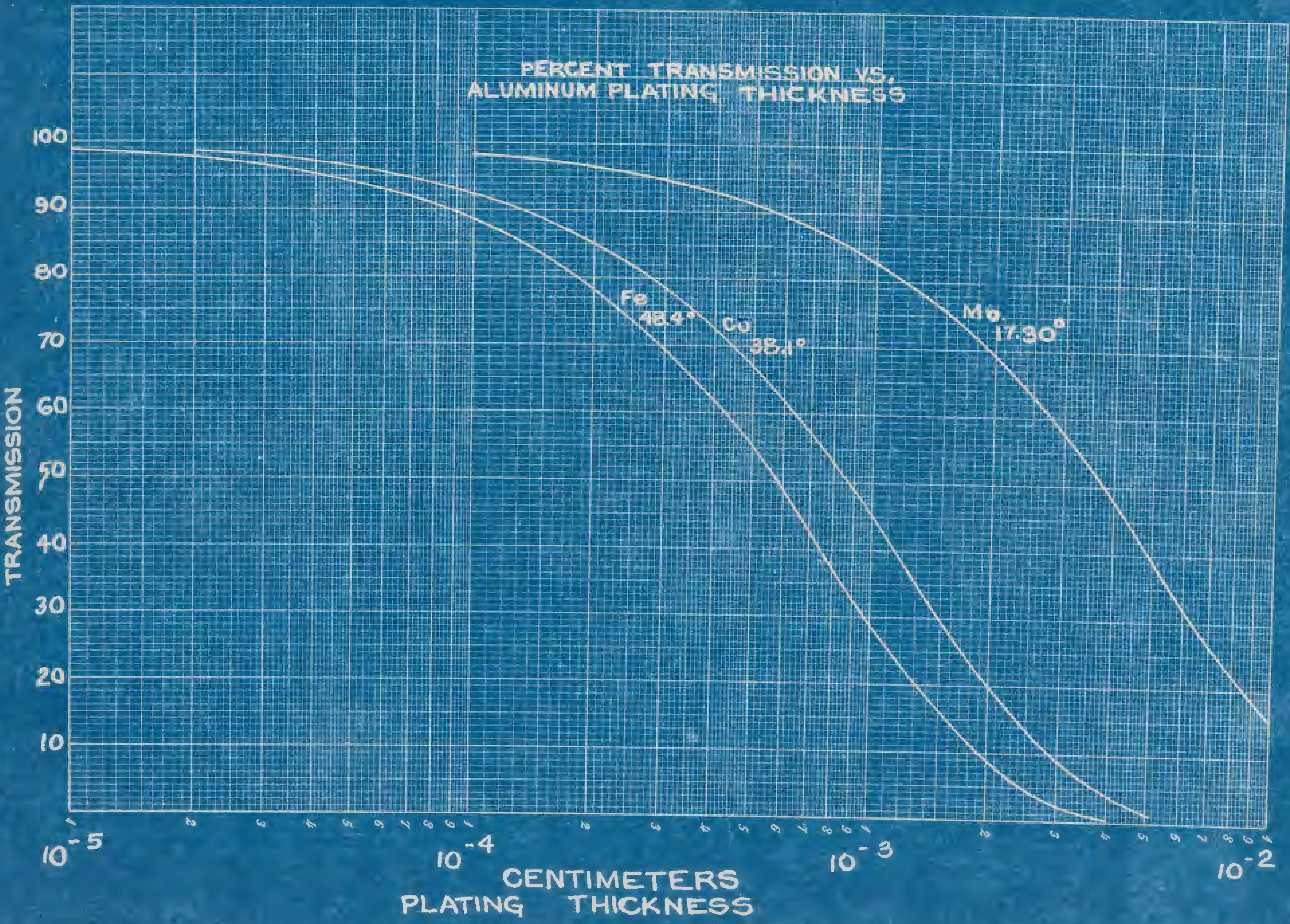
PERCENT TRANSMISSION VS.
ALUMINUM PLATING THICKNESS
TRANSMISSION
100
90
80
70
60
50
40
30
20
10
10^{-5}
10^{-4}
10^{-3}
10^{-2}
CENTIMETERS
PLATING THICKNESS
Fe 48.4°
Cu 38.1°
Mo. 17.30°

PLATE 3