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SUBJECT

THE CHEMICAL TREATMENT OF SILVER CHLORIDE SHEETS

TO PRODUCE FILTERS TRANSMITTING THE FAR INFRA-RED

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NAVAL RESEARCH LABORATORY

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NAVY DEPARTMENT

Report on

THE CHEMICAL TREATMENT OF SILVER CHLORIDE SHEETS
TO PRODUCE FILTERS TRANSMITTING THE FAR INFRA-RED

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ABSTRACT

Filters for transmitting the far infrared have been made by chemically treating rolled sheets of silver chloride to produce black powder films of silver sulphide or hard smooth films of silver sulphide. The optical properties of the filters have been measured, and it was found that suitable opacity at 1 or 2 μ can be produced while high transmission at 9 to 12 μ is maintained. The silver sulphide filters were found not to afford complete protection of the silver chloride from sunlight, but to afford sufficient protection to make them useful in many cases. Other films, chemically produced, are described. Only the silver sulphide films appear useful.

INTRODUCTION AND SUMMARY

This report describes experiments in which rolled sheets of silver chloride made by the Harshaw Chemical Company were coated with various substances formed by reactions with the AgCl itself with the view of obtaining the following properties:

- (a) The coating must be transparent to long wave-length radiation in the 8.5 to 12 micron region.
- (b) It must be opaque to ultraviolet and short wave-length visible light for the purpose of preventing reduction of the AgCl by interaction with daylight.
- (c) It is desirable that the material exclude all wave-lengths up to 2.5 or 3 microns in order that it may serve the double purpose of protective coating for AgCl and filter for excluding the major part of the solar infrared spectrum as well as the visible.
- (d) It should be unaffected by sea water.
- (e) It should be mechanically rugged so that it will not flake off easily.

This investigation was begun because of interest in the excellent optical properties of AgCl coated with a powder film of silver sulphide prepared by the Harshaw Chemical Company under contract with the Bureau of Ships, 660d.

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Summary of Results

Four coating materials gave good results.

Hard Silver Sulphide

Plate 1 is a typical transmission curve of a sample of this material prepared by dipping AgCl into dilute sodium sulphide. Its greatest advantage lies in its resistance to rubbing. Forty hours in the ultraviolet weatherometer reduced its 9μ transmission from 71 to 67 percent. A sample placed out-of-doors for a week was practically unchanged spectrally; it is not greatly affected by salt water. Apparently its only disadvantage lies in its less usable spectral qualities. Transmission rises from zero at 1μ to 13 percent at 1.5μ and 20 percent at 2.5μ while the transmission peak at 9μ is only 72 percent. A hard silver sulphide prepared by evolution of hydrogen sulphide in the presence of the silver chloride sample was also very rugged but not suitable spectrally. A sample of it was opaque to the short wave-lengths, transmitting only four percent at 2.5μ , but at long wave-lengths the transmission was low, being thirty-five percent at 9μ .

Silver Sulphide Powder Films

Two types of powdery silver sulphide coatings were made.

- (a) Powder Film. This is the type of film first prepared by Harshaw by dipping AgCl in Ammonium Sulphide solution, and this coating produced the most favorable transmission characteristics. Plate 2, curves (a), (b) and (c) show the manner in which short wave-length cut-off can be controlled by increasing the thickness of the coating. The short wave-length cut-off was varied from 1μ to 3μ between curves (a) and (c) while long wave-length transmission dropped from about 84 percent, curve (a), to 60 percent, curve (c). It has generally been found that thin coats such as (a) produce higher transmission at 9 to 11μ than the value 80 percent for clear uncoated AgCl. Presumably, the silver sulphide reduces reflection losses at the surface.

Silver sulphide is not so readily reduced by ultraviolet light as silver chloride, but it will not withstand long exposure. Curve (d) shows the transmission of a sample like (a) after 24 hours exposure in the weatherometer which reduced long wave-length transmission to 58 percent, and curve (e) is for a similar sample exposed to sun and rain out doors for 1 week which reduced the transmission to about 10 percent.

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The powder film of silver sulphide is fairly easily wiped off, but nevertheless, it is more adherent than usual powder filters like magnesium oxide. When one section of the film is rubbed off the reduction to silver spreads rapidly from the exposed area to the remainder of the film.

Dipping in a dilute solution of Gilsonite in benzene provided some protection against abrasion and improved somewhat the resistance to ultraviolet light, but the transmission to $9 - 13\mu$ light was reduced to 72 percent. The Gilsonite coating moved the short wave-length transmission limit slightly to shorter wave-lengths by virtue of reducing the relative index of refraction at the surface of each silver sulphide particle.

A powder film of silver sulphide as originally prepared by Harshaw produced the best optical characteristics and it is expected that the protection it offers to light will be adequate for many uses.

(b) Sulphur-coated Powder Film of Silver Sulphide.

Curve (f), Plate 2, shows the transmission of a sample like sample (a) after coating with sulphur. The transmission was reduced to about 66 percent at long wave-lengths, but this sample was more resistant to ultraviolet light than unprotected silver sulphide. Fifty hours exposure in the weatherometer reduced the transmission to about 60 percent and 4 days out doors produced no change in transmission.

Mechanically, the sulphur on silver sulphide coat was very rugged.

Silver Oxide

Typical spectral transmission curves of AgCl coated on both sides with hard smooth black films of silver oxide are shown in Plate 3. Curve (a) for a thin coat shows that transmission began in the deep red and rose to 84 percent at 11μ . The broad absorption band near 6μ is possibly due to water. In other cases where samples were more thoroughly dried, pronounced absorption in the 6μ region was not observed.

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Curve (b) is the transmission of a thicker sample which was opaque to about 1.5μ and which transmitted about 73 percent of the 9 to 10μ light. The transmission dropped to 60 percent at 12μ .

The good mechanical properties of silver oxide are accompanied by high sensitivity to ultraviolet light. Curve (c) is the transmission of sample (b) after 2 hours exposure in a weatherometer where it was subjected to ultraviolet radiation from a carbon arc and to continuous non-saline water spray. The transmission fell to 52 percent in the 9 to 10μ region. Twenty-five hours exposure in the weatherometer reduced the long wave-length transmission to 5 or 10 percent. Less than 2 days exposure to sunlight reduced the coating to silver and the transmission to very low values. However, ordinary room light does not alter it greatly.

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PREPARATION OF COATINGS

The chemical preparation of most coats on silver chloride is quite difficult because silver chloride is such a stable compound chemically. Replacement reactions were made use of, in which the chloride ion was replaced by a negative ion which, with silver, forms as stable a compound chemically as the chloride.

Silver Sulphide Powder

Silver chloride dipped in a very dilute ammonium sulphide solution produced the powdery sulphide coat. It was found that a coat which required forty-five seconds to become practically opaque to the visible radiation from a hot tungsten filament, produced optimum results. The longer the time of formation, the higher the short wave-length cut-off but where periods much longer than forty-five seconds were required, pinholes developed in the coat.

Sulphur-Coated Silver Sulphide

A layer of sulphur was produced on a silver chloride sample which had been previously coated with powdery silver sulphide by dipping the sample into a sulphur-saturated carbon disulphide solution and quickly withdrawing it. The carbon disulphide evaporates leaving a hard shiny layer of sulphur behind.

Hard Silver Sulphide

The hard shiny silver sulphide was obtained by dipping into a dilute solution of sodium sulphide. A higher wave-length cut-off was produced here by a long period of formation and no trouble with pinholes was encountered. Also, a shiny silver sulphide coat was obtained by holding the sample over a test tube in which hydrogen sulphide was being evolved by action of acid on sodium sulphide but the coat prepared by the first method was of higher transmission.

Silver Oxide

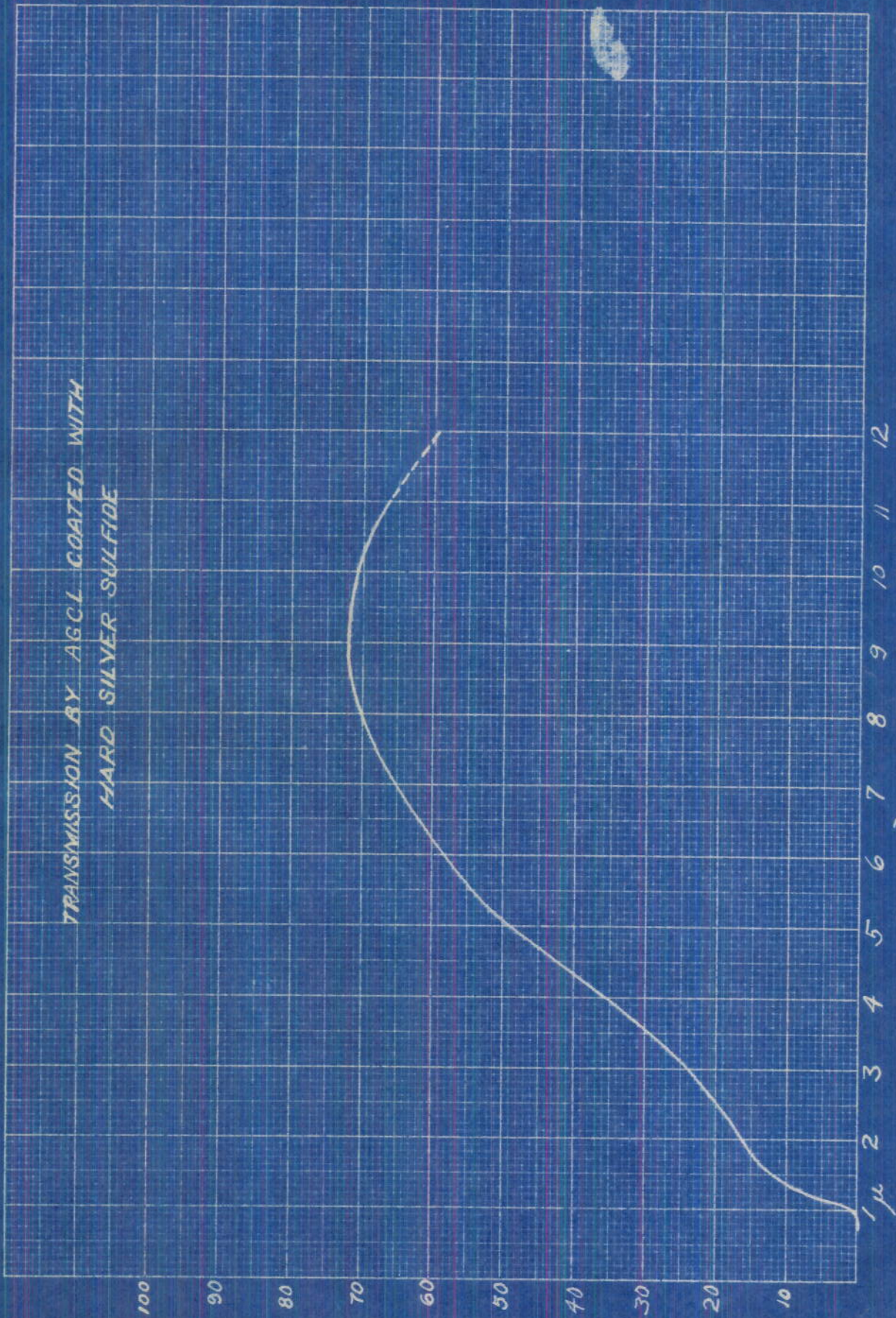
Silver Oxide was prepared by the action of dilute sodium hydroxide on silver chloride. The same optimum conditions of formation seemed to hold true here as for the sulphide. A powdery oxide coat was obtained by mixing ammonium hydroxide with sodium hydroxide, but its 9th transmission was only about sixty-five percent and it was reduced even more than the shiny oxide film.

MISCELLANEOUS COATINGS

What were presumed to be silver pyrophosphate and silver ferrocyanide coatings were prepared by dipping silver chloride sheets in hot solutions of sodium pyrophosphate and ferrocyanide but the pyrophosphate was not opaque even in the visible region and the ferrocyanide gave only about forty-five percent transmissions at long wave-lengths. Other films were prepared by boiling selenium and tellurium in solutions of sodium hydroxide just concentrated enough to dissolve some of the metal (enough to color the solution). When silver chloride was dipped into these solutions, the oxide of silver and probably the selenite or tellurite were formed. Then by dipping the sample in acid, the oxide was dissolved off. The selenite was prepared much more easily than the tellurite. The selenite was also prepared free of the oxide by neutralizing the basic sodium selenite solution with acid before dipping in the silver chloride sample. The 9μ transmission of each was only about 65 percent and the coats were reducible by ultraviolet. All four of the above mentioned coats were difficult to obtain and were probably not very pure chemically so that the reduction by light may have been due to a large extent to impurities such as the oxide.

Double replacement reactions were also made use of to obtain other coats but none gave desirable results. Mercuric sulphide was prepared by treating a silver sulphide coat with a hot concentrated mercuric nitrate solution but a coat was obtained which did not retain high transmission after exposure to ultraviolet light. Zinc, tin, copper, cadmium and iron oxides were all obtained by treating silver oxide samples with hot concentrated solutions of the nitrate of the metal. Iron oxide was not useful, for a sample coated thinly transmitted only forty percent at 9μ while one coated more thickly transmitted nothing. The zinc and copper oxide transmission maxima were at about 8μ where each transmitted from sixty-five to seventy percent. These two films were of the best transmission and protected the silver chloride from reduction the most successfully of any in the miscellaneous group. Thirteen hours in the weatherometer reduced the zinc oxide transmission to twenty-eight percent and the copper oxide to twenty-two percent while that of silver oxide was being reduced to twelve percent. The tin oxide transmission was reduced from fifty-six to five percent, and cadmium oxide from 60 percent to 17 percent. Mechanically the copper oxide coat is the most rugged. All of the oxide coats were practically opaque to 1.5μ or 2μ . At 2.5μ the zinc oxide sample transmitted eleven percent, cadmium oxide fifteen percent, and copper oxide twenty-one percent.

TRANSMISSION BY AGCL COATED WITH
HARD SILVER SULFIDE

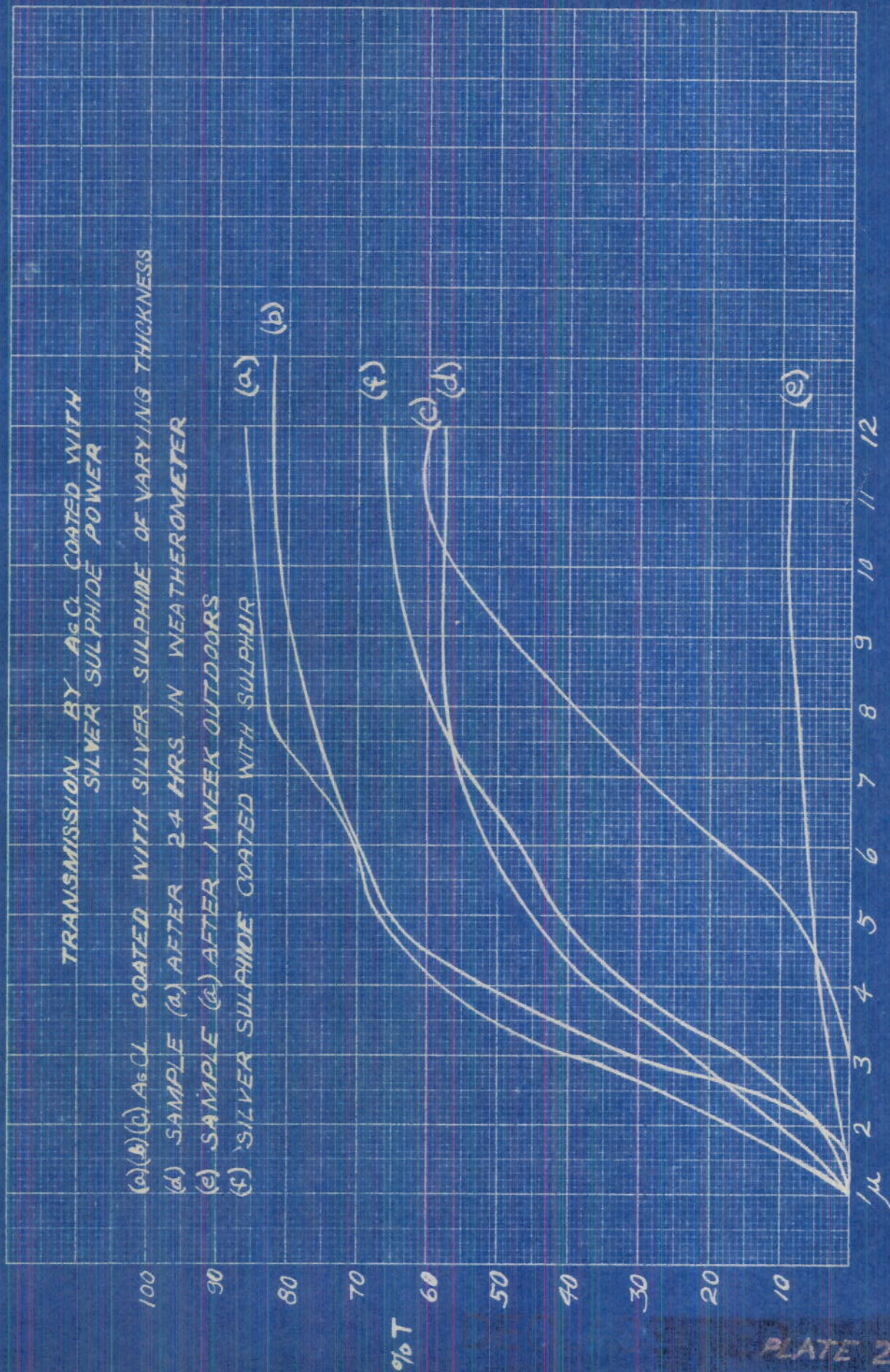


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PLATE I

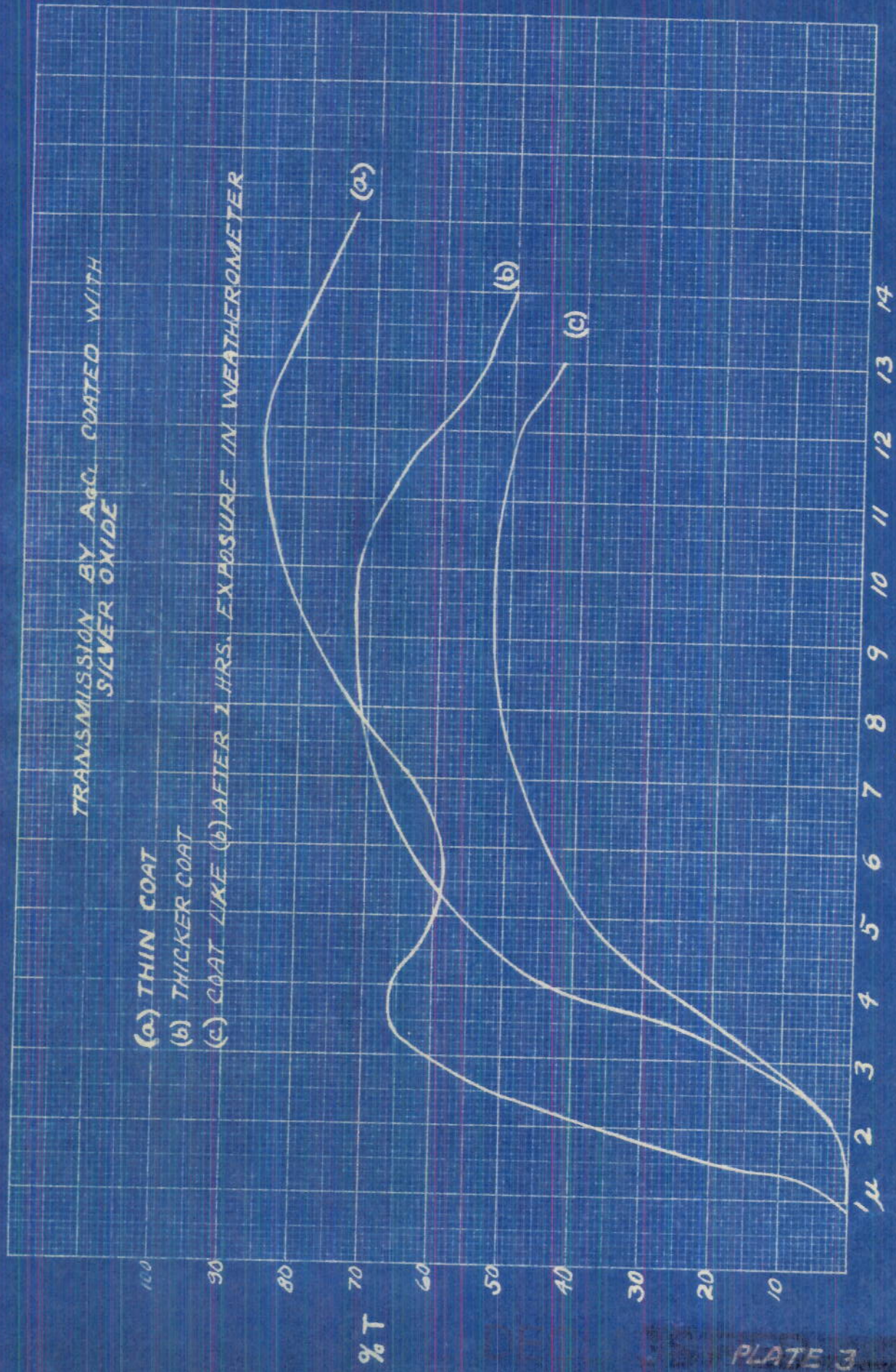
TRANSMISSION BY $AgCl$ COATED WITH SILVER SULPHIDE POWER

- (a)(b)(c) $AgCl$ COATED WITH SILVER SULPHIDE OF VARYING THICKNESS
 (d) SAMPLE (a) AFTER 24 HRS IN WEATHEROMETER
 (e) SAMPLE (a) AFTER 1 WEEK OUTDOORS
 (f) SILVER SULPHIDE COATED WITH SULPHUR



TRANSMISSION BY AgCl COATED WITH SILVER OXIDE

- (a) THIN COAT
- (b) THICKER COAT
- (c) COAT LIKE (b) AFTER 1 HRS. EXPOSURE IN WEATHEROMETER



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