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ZINC BROMIDE SOLUTION FOR USE IN SHIELDING WINDOWS

by

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# ZINC BROMIDE SOLUTIONS FOR USE IN SHIELDING WINDOWS

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William B. Doe

## I. INTRODUCTION

Large-area dense-material shielding windows are useful for viewing into enclosures containing high levels of radiation. They are particularly desirable when used in conjunction with rapid manipulators, such as the master slave type developed at Argonne. In this application the operator is not confined to a fixed eyepiece nor does he have to make any scanning or focussing adjustments as is usually necessary with periscopes. The use of shielding windows avoids the long observer-to-object distance and large openings in the shield usually necessary with viewing systems using mirrors. A short observer-to-object distance is necessary to permit good depth perception.

Large-area windows also permit one or more observers to rapidly scan a large working volume. Trouble at any point in the enclosure can immediately be recognized. This is not the case when using periscopes having a limited field of view. Wide-field periscopes can be made having a field of view as large as windows, but unless the operator is actually looking through the eyepiece he would not be immediately aware of any difficulties occurring inside the enclosure.

Transparent shielding windows can be divided into two classes: the solid type, which is usually a series of glass plates or cast blocks, and the liquid type, which is essentially a rectangular liquid-filled tank closed at two ends with glass cover plates. The usual dimensions would be about 30" x 36" with a thickness of several feet. Windows containing dense materials may sometimes be as thick as six feet.

Factors affecting the design of glass and zinc bromide-filled shielding windows have been outlined.<sup>1</sup> Specifications for nonbrowning glass to be used in glass-filled windows and for cover plates on the "hot" side of liquid-filled windows have been written.<sup>2</sup>

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<sup>1</sup>A Manual of Remote Viewing, ANL-4903 (August 11, 1952).

<sup>2</sup>"Tentative Specifications for Nonbrowning Lime Glass for Shielding Windows," August 15, 1950, Argonne National Laboratory.

Water frequently has been used as a liquid shielding material. For underwater operations where viewing is downward into a "canal" or through ports in the side of a tank, water makes a cheap and satisfactory shield. Where dry operations are necessary at moderate to high radiation levels, water-filled windows have many disadvantages. Because of the low density of water, such windows must be very thick, in some cases as much as 18 feet. In order to obtain a wide field of view, the glass cover plates must be excessively large. The long distance from observer to object results in poor depth perception. Since most shielding walls are at least as dense as concrete (sp. gr. 2.3), the windows must be  $2\frac{1}{3}$  times as thick as the walls. This requires the construction of awkward transition pieces around the protruding window. Thus, except for installation encountering low radiation levels, the low cost of water is more than offset by the increased cost of construction, larger floor space requirement, and resulting poor depth perception.

In general, the shielding power of a substance for hard gamma rays is proportional to its density only and does not depend on the composition of the substance. Greater density, then, means thinner windows. In addition, denser substances usually have a higher index of refraction for light. A window made of higher refractive index material will be smaller in frontal dimensions for a given field of view because of the bending of the light rays. High refractive index will also make an object appear closer to the observer than it really is.

For shielding X rays or other soft radiation, a solution of lead acetate in water has been used. The density of this mixture is about 1.5; however, the shielding power is somewhat greater than the density would indicate. The photoelectric effect for elements of high atomic weight is significant when soft radiations are being considered; hence in this case both the atomic weight and density determine the shielding power.

Acetylene tetrabromide with a density of 2.9 was investigated as a shielding material by K. R. Ferguson.<sup>3</sup> Its poor stability to radiation and light was greatly improved by the addition of the stabilizer recommended by the manufacturer.

It was abandoned in favor of zinc bromide (density 2.5) because of handling problems relating to its toxicity and immiscibility with water.

Since shielding walls are often built of magnetite or barium ore-loaded concrete with a density of about 3.2, some preliminary work has been done on solutions which would permit the construction of a liquid-filled window to match a wall of this density. Anhydrous tin tetrabromide mixed with tin tetrachloride was a liquid at room temperature, had a density of 3.2, and was found to be resistant to radiation. Unfortunately it cannot be allowed to come in contact with moisture, and so would be difficult to handle.

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<sup>3</sup>ANL-4246, February, 1949, p. 23.

A solution of barium and mercuric bromides in water also had a density of 3.2. Exposure of this solution to one million roentgens of gamma radiation had no noticeable effects. The amount of haze observed in the laboratory sample may be objectionable if encountered in a large window. Both of the above solutions (density 3.2) require further investigation in order to develop a solution which would be satisfactory for use in shielding windows. The cost of these materials would probably be at least \$2.00 per pound.

Zinc chloride (density 1.89) has been considered but rejected because of its low density. It could probably be manufactured in optical quality and stabilized to radiation as has been done with zinc bromide.

Other materials have been considered, such as methylene bromide, cadmium borotungstate, thallium formate-malonate, and others reported by the Bureau of Mines for mineralogical analysis.<sup>4</sup> In general, these were too costly to compete with glass-filled windows.

In 1948 the Remote Control Engineering Division became interested in building large windows. Preliminary work indicated that concentrated solutions of zinc bromide would be the best choice as a shielding liquid. A commercial grade of solution had been manufactured for use in the rayon industry. Some investigation into the use of zinc bromide for shielding windows had been done at the Oak Ridge Laboratory.

Several windows up to 3 feet thick were built at Argonne using a specially clarified commercial grade of zinc bromide solution. Glass windows made of a series of 1 inch thick plates were also constructed using chemically pure zinc bromide as a laminant for reducing surface reflections. All of these solutions deteriorated in use, and periodic refiltrations were necessary. In 1950 an intensive program to improve the quality and dependability of zinc bromide windows was initiated. Factors affecting the chemical stability and radiation stability were determined. Several suggestions as to modifications in manufacturing procedure resulted in improvements in the commercial product. Continuing efforts by the manufacturer to improve the quality have produced a solution far superior to those used in 1949 and 1950. Periodic refiltration is no longer necessary. Windows which are completed or under construction at the present time will consume more than 7000 gallons of zinc bromide solution. Window thickness is not now limited by transmission for light but by gassing effects in the solution produced by the intense radiation encountered in thick window installations. This problem is being investigated. If it can be controlled, windows as thick as 9 feet should be possible.

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<sup>4</sup>John D. Sullivan, "Heavy Liquids for Mineralogical Analyses," Bureau of Mines Technical Paper No. 381, Govt. Printing Office, Washington, D.C., 1927.

## II. CHEMICAL STABILITY

### A. Effects from Oxidation by Air

One of the first difficulties encountered in zinc bromide solutions was the formation of a yellow color or orange precipitate in a solution that was initially clear. Removal of the precipitate by filtration was only a temporary solution to the problem. The filtered solution would soon again become cloudy. The precipitate that formed was found to contain ferric iron and is undoubtedly ferric hydroxide formed by the oxidation of ferrous iron. Some of the first batches of zinc bromide contained as much as 1500 parts per million of ferrous iron.

K. R. Ferguson investigated the use of orthophosphoric acid to control the ferric iron.<sup>5</sup> This was effective in preventing the color and precipitate, but on long standing quantities of a gel formed in the solution. The use of this reagent has been discontinued.

Solutions which had been stabilized with phosphoric acid frequently developed a white haze. Since the odor of hydrogen sulphide was noted when these solutions were acidified, it was thought that the haze was caused by sulphide ion being oxidized by air to free sulphur. The effect was reproduced in chemically pure zinc bromide by adding known quantities of sulphide.

It was suggested to the manufacturer that sulphide and ferrous iron could be eliminated if the solution were oxidized by adding bromine before the final filtration. This was done in all batches manufactured after about December, 1950 and resulted in the complete removal of sulphide and a reduction of the total iron content from the usual several hundred parts per million to only several parts per million.

### B. Hazes Formed from Supersaturated Solutions

Elimination of the precipitates formed by air oxidation allowed precipitates occurring in less quantity to become visible. A series of windows was constructed in early 1951 in which a white haze appeared after several weeks. The haze continued to increase for about six months. At the end of a year it had settled to the bottom, and the windows were completely clear. At no time were the windows unusable; however, the loss of contrast made work difficult in shaded areas of the enclosure. Collection of a sample of the haze by filtration was not possible because of the small quantity. The material which had settled from 150 gallons of zinc bromide was siphoned off to yield about a gallon of zinc bromide rich in haze. This was settled for several months, and a second concentrate centrifuged to yield a fraction of a gram of solids. Spectrographic and wet analysis showed that the haze was calcium sulphate containing

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<sup>5</sup>"New Hot Laboratories at Argonne," ANL-4385 (October, 1949).



about 10% strontium and some barium. Subsequent experience has shown that this sulphate type of haze may result from the mixing of a batch of zinc bromide high in sulphate with one high in alkaline earths. The manufacturer has taken steps to minimize the possibility of sulphate haze formation. However, this problem has not been completely solved. In general, recent batches have not developed a sulphate haze. In only one out of six recently constructed windows has even a moderate amount of haze developed. This type of haze may be recognized by its insolubility even when the solution is strongly acidified.

In the latter half of 1951 a new type of haze was encountered. This was a white haze which formed after a few weeks, particularly when the solution was exposed to air. Analysis showed that it contained iron. It was found to dissolve when the alkalinity (defined in the Specifications, Section IV D of the Appendix) of the solution was reduced to 8. The ferric hydroxide type of haze previously discussed dissolves at an alkalinity of zero.

Since all of these batches had an alkalinity of about 35 (highly alkaline), it was thought that the precipitate was a basic ferric bromide formed from the few parts per million of iron remaining in the improved solutions. Exposure of the solution to air causes the haze to increase because of conversion of some ferrous to ferric iron. As will be explained under "Radiation Stability," optical grade zinc bromide must contain a reducing agent to prevent certain oxidation effects. In the presence of this reducing agent at an alkalinity of not more than 16, the reduction of iron proceeds at a reasonable rate. Hence, the basic ferric precipitate will be controlled. A specification was written to insure that the solution would be manufactured with the proper alkalinity.

It is necessary to add the reducing agent soon after manufacture of the solution because, once formed, the basic iron precipitate may require several months to be reduced and redissolved.

In order to avoid the appearance of new unknown hazes, a study was made of common elements which would be expected to form highly insoluble compounds. The results are shown in Table I. Time for formation is only approximate since it depends somewhat on the concentration of the element.

Aluminum remains in supersaturated solution for such long times that insufficient data have been collected to determine the solubility of the haze. Arsenic and antimony are suspected as haze formers but have not been investigated. Elements which did not form a haze at a concentration of 500 parts per million were lead, silver, magnesium, nickel, cobalt, manganese, and the alkali metals as well as tin, copper, and iron in their lower valence states.

TABLE 1

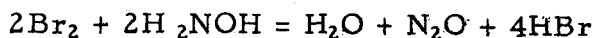
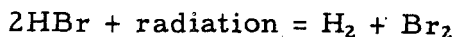
Element	Approximate Amount Added to Form Haze (Solution Alkalinity was 16)	Time for Formation	Alkalinity at which Haze Dissolves
<u>Sulphate Type</u>			
Ca	2 ppm	Several days	none
Sr	1	Several days	none
Ba	1	Several days	none
<u>Hydroxide Type</u>			
$Fe^{+3}$	1-5	Several months or longer	-0.5
$Cr^{+3}$	1	A few hours or less	3
Al	5 (rough estimate)	Several weeks or months	4
$Sn^{+4}$	large amounts	One day?	?
$Cu^{+2}$	less than 50	Two days or less	12
<u>Elemental Sulphide</u>	1	Immediately	none
<u>Basic <math>Fe^{+3}</math></u>	5	Several weeks (alkalinity of the solution was 35)	16
<u>Anion</u>			
$SO_4$	800	Precipitation of $ZnSO_4$	--
$PO_4$	large amounts	Slow formation of a nearly invisible gel	--

The alkaline earth sulphate type of haze is the only known haze which is not completely controlled in optical grade zinc bromide. Chromium is extremely insoluble and precipitates rapidly. It is probably completely removed in manufacture at the time iron is removed. Iron and copper are maintained in the reduced state by the stabilizing agent added after manufacture and so do not form hazes. Sulphide is removed in manufacture by oxidation. Aluminum, arsenic, antimony, and tin have never given trouble and hence are probably not present in sufficient concentration to produce haze. Carbonates are decomposed in zinc bromide; hence  $CO_2$  in the air does not produce a haze.

Optical grade zinc bromide can be diluted with distilled water without causing a haze or other objectionable effects. Large dilution will produce a zinc hydroxide precipitate.

### III. RADIATION STABILITY

The action of ionizing radiation on zinc bromide solution is to liberate hydrogen gas, resulting in a net oxidizing effect on the solution. Impurities such as sulphide or iron are oxidized with the same result as is produced by air oxidation. If easily oxidized impurities are absent, radiation will oxidize the bromide ion to free bromine. When it was learned that phosphoric acid was not satisfactory for controlling ferric iron, a search was begun for an iron reducing agent which would be colorless in both the reduced and oxidized form. The sulphide ion is very effective in reducing iron but can immediately be ruled out because its oxidation product is a free sulfur haze. Sulphite was not effective. Formaldehyde gave only partial reduction. Arsenite reduced the iron slowly but produced a haze. Stannous tin was very effective, and the haze formed from stannic tin could be controlled by acidifying the solution. Unfortunately stannic tin produces strong absorption in the violet part of the spectrum. Hydroxylamine hydrochloride was found to be completely effective and introduced no color or haze. This reagent absorbs the oxidizing effects of the radiation probably by becoming oxidized to water and nitrous oxide.



The actual mechanism of radiation induced reactions in zinc bromide is unknown. In one experiment the oxidizing power of  $\text{Co}^{60}$  radiation for zinc bromide solution was found to be  $8.9 \times 10^{-3}$  equivalents per  $10^6$  roentgens per liter. This assumes that the sample is thin enough so that the attenuation of the radiation is not appreciable in passing through the sample. Assuming that an equivalent weight of hydroxylamine hydrochloride is one-half the molecular weight, adding 4 ounces per 100 gallons of zinc bromide solution would protect it from  $10^6$  roentgens of incident radiation when exposed as a small sample. The radiation intensity falls off rapidly as it proceeds through a large window. Unexposed liquid in the rear area of the window will slowly be thermally stirred to the front section to replace the exhausted solution. With  $\text{Co}^{60}$  radiation on a 3 foot thick window the stabilizer becomes about 10 times as effective because of this mixing. Thus the addition of 4 ounces of hydroxylamine per 100 gallons of zinc bromide as recommended in Appendix II of the Specifications will protect a window from a total incident dose of at least  $10^6$  roentgens, or  $10^7$  roentgens, if the dose is extended over a period sufficiently long to allow thermal mixing to occur.

It was found that after a one-year test hydroxylamine does not spontaneously decompose to any great extent in zinc bromide. Hydroxylamine will not prevent the sulphide ion from being oxidized by radiation. There is reason to believe that without hydroxylamine, part of the sulphide is oxidized to sulphate. Hydroxylamine appears to increase the fraction going to free sulphur and hence produces more haze than if it were absent. Complete removal of sulphide during manufacture is therefore essential. A dose of  $10^6$  roentgens in 24 hours in a small sample is known to produce an appreciable quantity of nitrous oxide bubbles. This is an intensity of  $4 \times 10^4$  roentgens per hour and is the maximum rate without serious gassing. If one assumes  $8 \times 10^{-3}$  roentgens per hour is permitted on the "cool" side of the window, the window attenuation in this case would be  $5 \times 10^6$ . Using 2.5 inches of zinc bromide as a half value layer, the maximum thickness of a zinc bromide window would be 55 inches. Thermal mixing of the solution would dilute the supersaturated layer at the "hot" side and may permit a somewhat higher irradiation rate. This would place the upper limit of window thickness near five feet. Large-scale experiments would be necessary to determine to what extent the amount of gassing to be encountered in a five-foot window would obscure vision. Experiments are now under way to clarify this point.

Reduction rate of iron by hydroxylamine is a function of alkalinity. The maximum rate occurs at an alkalinity of 2.7 where reduction of 10 ppm of ferric iron with 100 ppm hydroxylamine at room temperature is essentially complete in 3 minutes. At an alkalinity of 5.6 the reaction requires several weeks. At the specification limit of 16 alkalinity, reduction is complete in a month or two. A ferric precipitate was not reduced by hydroxylamine in 4 months when the alkalinity was 35. In acid solution the reduction rate appears to be slow but this has not been studied.

The reduction of iron with an excess of hydroxylamine is proportional to the logarithm of the time; hence total reduction is approached very slowly as the reaction nears completion. Cupric copper and free bromine are almost instantly reduced by hydroxylamine. Oxidation of cuprous copper results in a brown color followed by precipitation of the green hydroxide. As long as hydroxylamine is present copper ions will not be oxidized by radiation.

Tin, arsenic, and antimony are probably not protected from radiation by hydroxylamine although this point has not been specifically studied. We have not experienced any difficulties with these elements in the commercial solutions.

#### IV. LOW-TEMPERATURE STABILITY

In order that zinc bromide may be shipped in the winter in the same manner as other freezable items, the density specification has been set up to insure a freezing point near  $32^\circ\text{F}$ . In October, 1951, before an alkalinity

specification was written, we encountered batches of zinc bromide of the proper density but with an unusually high freezing point of 40°F. These were the same batches that developed a basic ferric haze. Crystals which had separated in long needles were collected and titrated with acid. The results indicated that the crystals were basic zinc bromide. These batches were found to have an unusually high alkalinity of 35. Freezing point as a function of alkalinity is shown in Figure 1.

Highly alkaline solutions had two freezing points. The lower one was obtained by cooling the solution in dry ice and gradually warming until crystals formed. The temperature was allowed to continue to increase with constant stirring. The freezing point (melting point) was taken as the temperature at which the crystals (normal salt) had just gone into solution. The plotted point at 30°C. was obtained by allowing the solution to stand several hours until crystals formed (basic salt) and is the actual freezing point or crystal point of the solution. These crystals were not analyzed but had the appearance of basic zinc bromide. Because of the reluctance of the basic salt to crystalize, only the one point at 30°C. could be obtained.

The alkalinity and density specifications insure that the freezing point be within the crosshatched area. The high alkalinity limit was set at a value which would allow a reasonable reduction rate of the basic ferric haze by hydroxylamine. The lower limit was set so that the solution would not be more acid than that of the solution in which corrosion tests had been run. Highly acid solutions, particularly with phosphoric acid, are known to attack stainless steel rapidly.

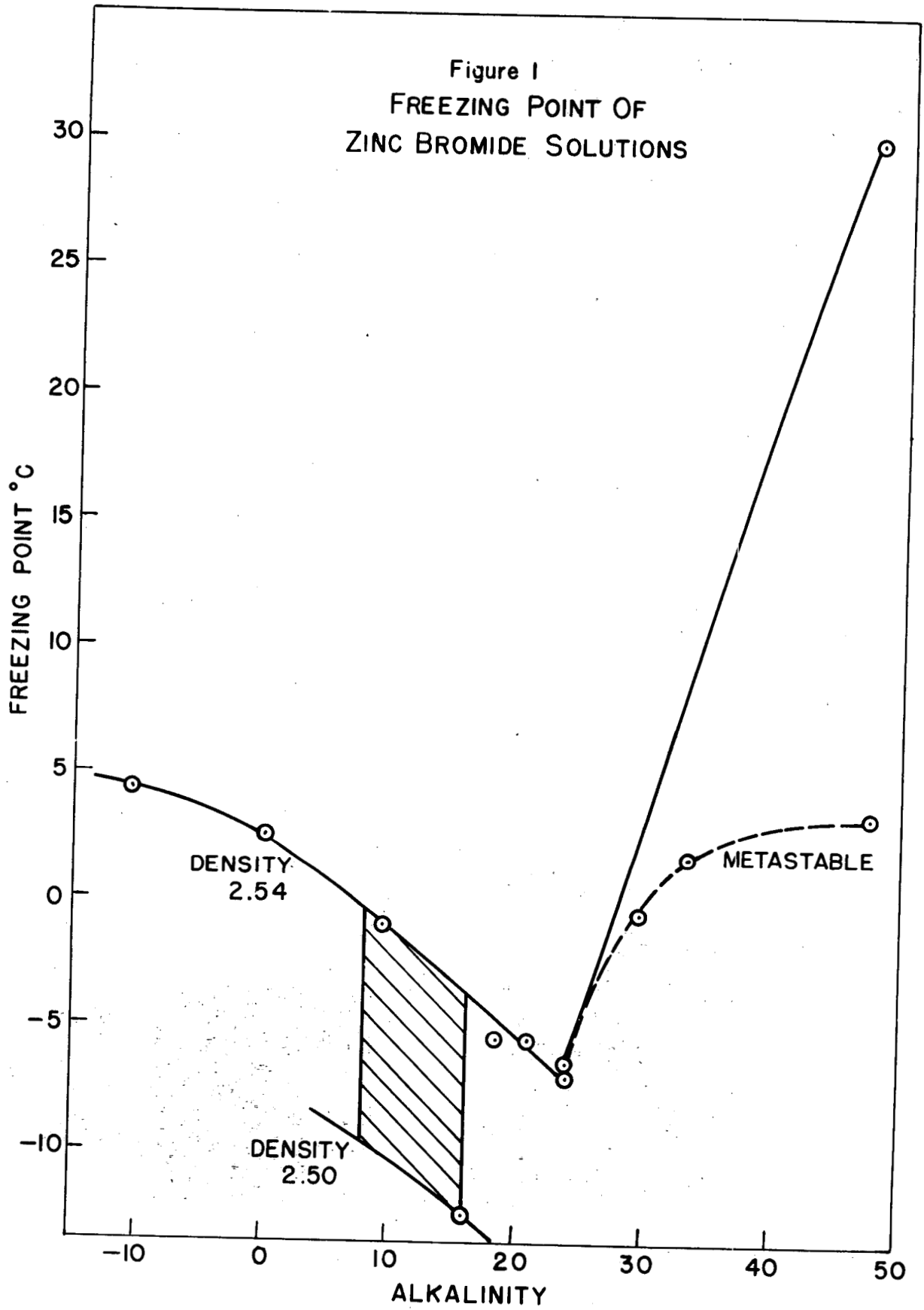
Variation of freezing point with density at an alkalinity of 16 is illustrated in Figure 2.

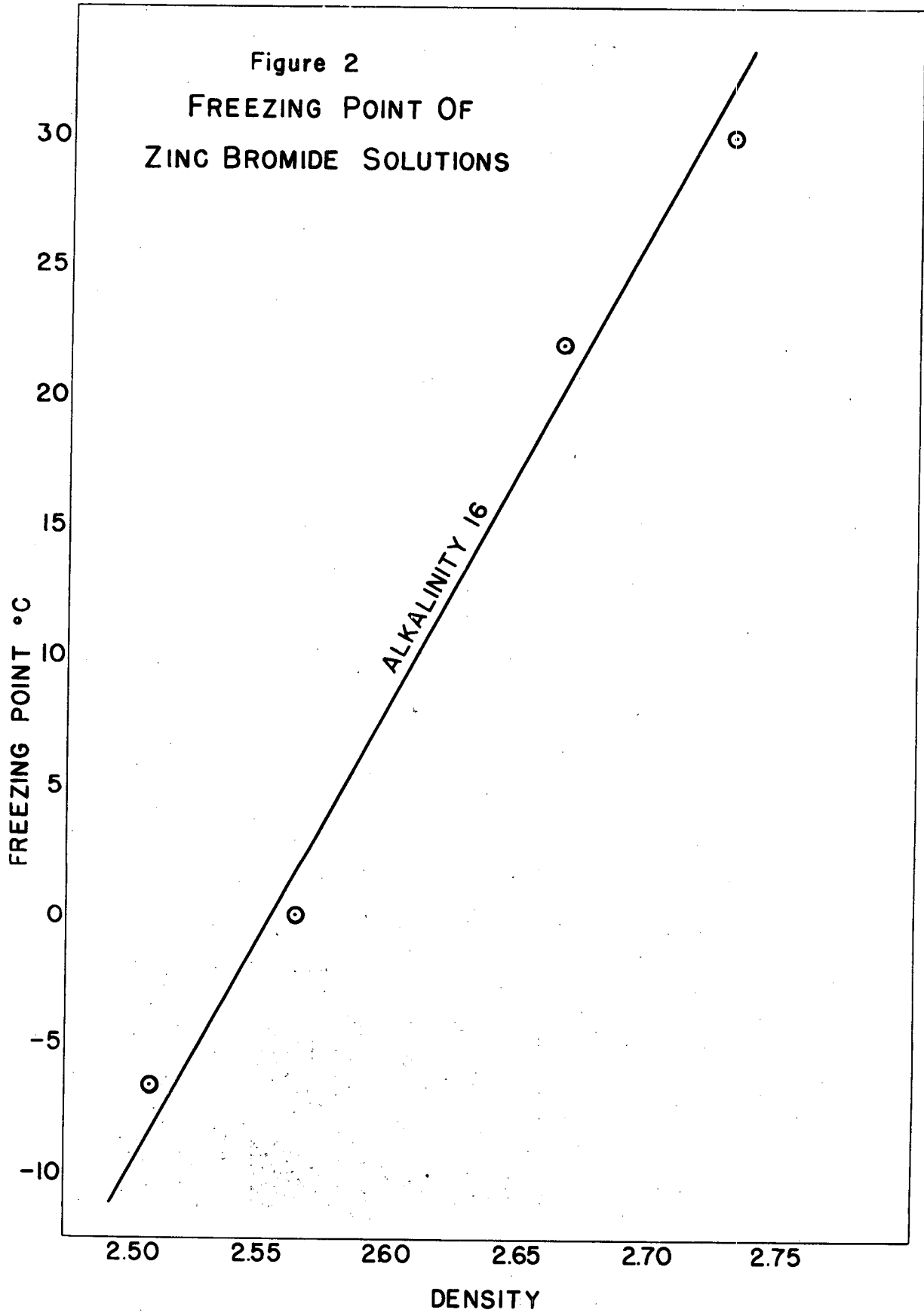
## V. OPTICAL TRANSMISSION

### A. Optical Transmission as Influenced by Metallic Ions

The degree to which the solution must be free of colored ions can be determined from Figure 3, where light absorption data for 5 centimeters of zinc bromide solution of zero alkalinity containing various elements are shown.

The data for chromium and ferric iron were included only as a matter of interest. Chromium is of such low solubility in the usual solutions with an alkalinity of 8-16 that its absorption spectrum cannot be detected. Ferric iron shows this intense absorption only in solutions of zero or negative alkalinity. In alkaline solutions ferric iron produces a much less intense yellow color. Fifty parts per million ferrous iron or 500 parts per million of manganese or cadmium produced no detectable absorption.





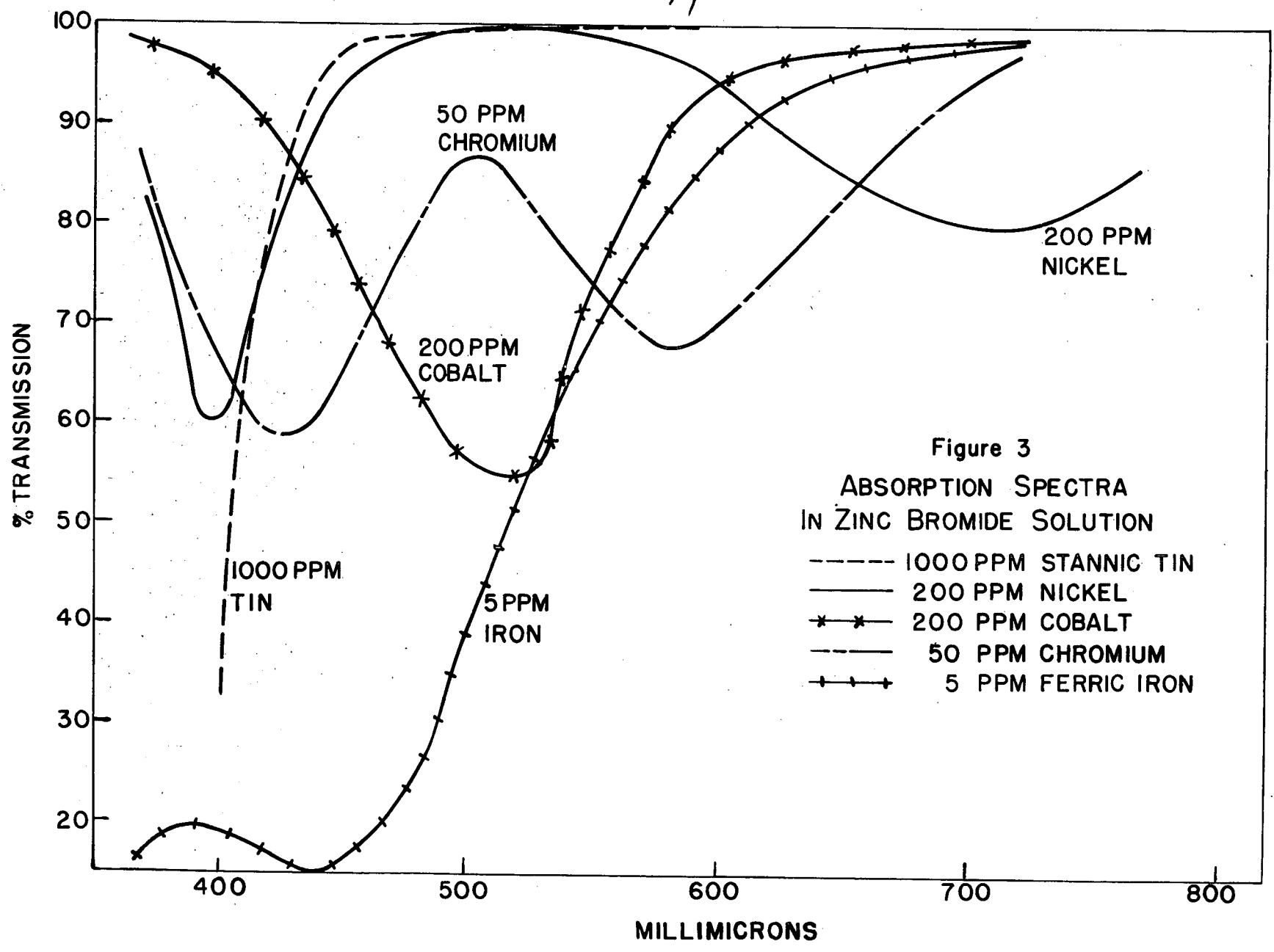


Figure 3  
ABSORPTION SPECTRA  
IN ZINC BROMIDE SOLUTION

- 1000 PPM STANNIC TIN
- 200 PPM NICKEL
- \* \* — 200 PPM COBALT
- 50 PPM CHROMIUM
- + + + 5 PPM FERRIC IRON

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Stannic tin produces absorption in the violet where the eye is insensitive and so would not have a large effect on the transmission of a window for white light. Its absorption for sodium vapor light would be negligible. Nickel and cobalt are soluble in alkaline zinc bromide and would certainly decrease the transmission of a window if present in sufficient quantity. Based on the assumption that cobalt is present in the usual proportion of about 1% of the nickel content, the loss in transmission of zinc bromide due to 10 parts per million of nickel with its associated cobalt can be calculated.

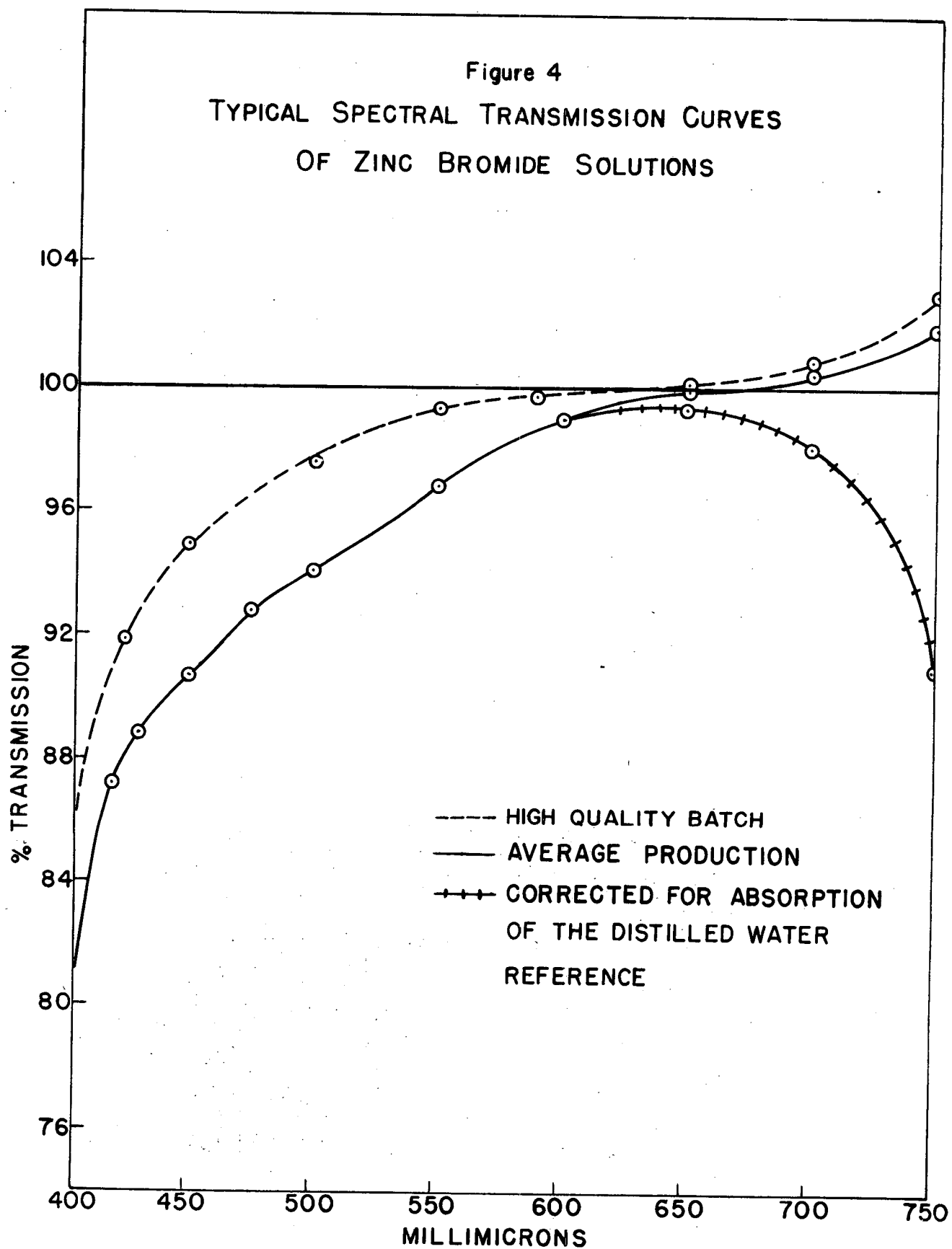
Absorption of 10 ppm Ni - Co	in 5 cm	in 3 feet
For sodium light	0.2 %	3.6 %
For solar light	0.16 %	2.9 %

The nickel in various batches of recently manufactured zinc bromide was precipitated with dimethyl glyoxime and weighed. The concentration varied from 0 to about 12 parts per million. Addition of 1 part per million of nickel to a nickel-free batch gave an appreciable precipitate, proving that the test was sufficiently sensitive.

Typical transmission curves referred to water for recently manufactured batches are illustrated in Figure 4. The "corrected" curve has been corrected for the absorption of the distilled water in the reference cell which becomes appreciable at wavelengths longer than 6000 angstroms. There are two other factors of less importance which result in the apparent transmission being different from the real transmission. The reflection at the silica window-zinc bromide and silica window--water interfaces of the comparison cell is not the same. With yellow light this difference amounts to less than 0.1%. The beam of light passing through the sample cell is slightly diverging in the Beckman Spectrophotometer. If liquids of different refractive indices are compared, an error results because of the different converging effects of the liquids. This error has not been measured, but transmission measurements on thick windows with other equipment indicate that it is small. The transmission of a thick window, therefore, may be computed without correction from measurements on small samples with reasonable accuracy except for wavelengths longer than about 6000 angstroms.

#### B. Optical Transmission as Influenced by Contamination by Container Materials

Windows have been constructed from #347 stainless steel which contains the rare element columbium. Spectrographic analysis of the precipitate from one of these windows showed that the precipitate contained considerable iron and chromium along with a half dozen other elements including columbium. Obviously the stainless steel was dissolving, causing the precipitate or at least contributing to its magnitude.



A series of windows was lined with 1/4 inch thick tank lining grade Koroseal. Preliminary tests had indicated that this material produced very little color in zinc bromide. After several months' exposure it was found that the plasticizer was bleeding. Grade 116 Koroseal was found to be fairly free of bleeding but could not be fusion welded for fabrication into a lining; however, this material is very satisfactory as a continuous gasket.

Tests were made to determine the most suitable material for lining zinc bromide windows and for handling the solution when filling windows. Table 2 shows the coloring of zinc bromide stabilized with hydroxylamine when 30 cubic centimeters of solution was exposed to samples of various materials whose surface areas were between 1 and 10 square inches.

TABLE 2  
CONTAMINATION OF ZINC BROMIDE SOLUTIONS  
BY CONTAINER MATERIAL: 1-YEAR EXPOSURE

	% Transmission at	
	4250 Angstroms	5890 Angstroms
Blank	93.3	99.1
Amercoat #31 Paint on steel	93.5	99.1
Small Sample of Polyvinyl rigid plastic	90.2	98.0
Silver	89.6	97.5
Baked Phenolic Coating on Steel (Lithgow Corp.)	85.3	97.6
Black Koroseal	84.5	97.3
White Tygon Sheet	84.3	97.6
Polyethylene (Sample 1)	80.5	97.5
Teflon	80.2	94.8
Black Tygon Sheet	79.9	96.8
"No-Ox-Id" Wax (Dearborn Chemical Co.)	77.5	96.2
Grey Koroseal	74.0	96.1
Tank Lining Grade Koroseal	73.2	96.1
Amber Koroseal	72.3	95.4
Amerplate Sheet (Amercoat Corporation)	72.0	96.1
Polyethylene (different source than sample 1)	62.9	91.6
Saran - clear film	60.4	92.1
Nickel	<u>1</u>	
Amercoat #55	<u>1</u>	
Sirvene Rubber (Chicago Rawhide Mfg. Co.)	<u>1</u>	
Silver Plate - 0.3 mill over copper on steel	<u>2</u>	

1 Transmission was so low that the test was discontinued.

2 Test was discontinued because of blistering and gassing at pinholes.

Transmission data were collected at 9 wavelengths every 3 months. Results at the other times and wavelengths were similar to those in Table 2. It is fortunate that Amercoat system 31 paint with the least coloring effect is perhaps the easiest to apply to a tank. In case of accidental damage the coating can very simply be patched. The test sample which was applied over mild steel showed no visible deterioration after 18 months' immersion in zinc bromide with an alkalinity of 5.

Two window tanks approximately a 3 foot cube in size made of mild steel were coated with Amercoat 31. After six months' service no pinholes or other defects in the coating were visible.

The manufacturer of Amercoat 31 recommends that all edges or corners on surfaces to be coated should have at least a 1/8 inch radius. A putty is available for filling corners. Surfaces should be freshly sandblasted before painting. A prime, three body, and three seal coats are alternately brushed and sprayed. The completed job should be given an electrical resistance test with a rag saturated with salt solution to locate pinholes. Crystal type headphones in parallel with the resistance meter produce an audible click when a defect is crossed. The spark test should not be used because the high voltage may pierce an otherwise satisfactory coating. This is true in this particular case because the body coats contain metallic lead particles.

## VI. CORROSION OF CONTAINER MATERIALS

The corrosion of most metals above hydrogen in the electromotive series is fairly rapid. Lead, even though it is the lowest member, is rapidly attacked with the liberation of hydrogen. Below hydrogen, copper and silver are slightly attacked. The corrosion rate of silver was determined at 50°C. by exposing several square inches of foil to zinc bromide solution for one year. Loss of weight indicated that the corrosion rate was 20 millionths of an inch per year.

The corrosion rate of copper is also believed to be low. A circular steel window was lined with copper by copper welding and hammering the resulting cylinder to expand it into place. No obvious corrosion has been observed after two years of service. A window with a copper expansion tank did show signs of corrosion at the liquid surface after one year of service; however, it is expected that the tank will last for many years. Copper and silver are the only two moderately expensive metals which can remain in contact with zinc bromide solutions for long times without bad corrosion or coloring of the solution.

Organic materials are practically unaffected by zinc bromide solution. Of all the organic materials tested the darkening of clear Koroseal and the bleeding of the plasticizer in other grades of Koroseal were the only signs

that an appreciable amount of deterioration was occurring. Unfortunately most organics cause various degrees of coloring of the solution.

A sample of Amercoat 31 in contact with stabilized zinc bromide was given a dose of  $10^7$  roentgens from cobalt-60. No deterioration of the coating was observed.

## VII. FILTRATION AND HANDLING OF THE SOLUTION

Concentrated zinc bromide solution if left in contact with the skin for several hours will produce blisters. If the exposure is only 5 or 10 minutes and the skin is rinsed with water, no particular damage will result. Diluted zinc bromide solution is relatively harmless.

Filter paper, cotton, and other fibers used in cloth are swollen and changed to a gel by concentrated zinc bromide. The usual asbestos and paper filter pads become nonporous and so cannot be used as a filter medium. Glass cloth and filter aid such as Johns-Manville High Flow Super Cel are very satisfactory. Sufficient filter aid is added to form about a 1/4 inch thick cake on the glass cloth in the first recirculating step at low pressure. The pressure should then be increased to about 15 pounds in order to compact the cake.

The solution should be recirculated until critical observation shows no cloudiness present. Three hundred square inches of filtering surface will give a flow of 10-20 gallons per hour at 25 pounds pressure. Since the time of contact in a filtering operation is short, a stainless steel plate and frame type of filter is permissible. A hard rubber gear pump capable of supplying 50 pounds pressure can be used for filtration and for transferring zinc bromide. The solution cannot be filtered directly into a window because air bubbles mixed into the solution by the pump and the usual pressure-regulating by-pass valve will collect on the glass where they are difficult to remove. A filtering setup has been built in which the pressure to the filter is regulated by adjusting the voltage to a special motor whose torque is nearly independent of speed. Since it is no longer necessary to filter optical grade zinc bromide, it has not been determined whether this equipment will operate without introducing bubbles.

Windows have been filled by blowing the solution from the carboys with air pressure. This procedure is even more dangerous than blowing usual liquids because of the high density of zinc bromide. The danger is reduced if the container is elevated so that the operation is essentially one of siphoning. The end of the delivery tube should be kept just below the surface of the liquid in the window to minimize introduction of air bubbles.

For filling windows from open head drums, a special cover with stainless steel valve and vent was constructed. With this bolted in place of the normal cover, the drum was hoisted above the window and the solution run out by gravity. Hoses for transferring zinc bromide may be extruded polyethylene tubing if the contact time is limited to a day or so. Clear Koroseal tubing can be used for one day only. Bleeding of the plasticizer in the clear grade of Koroseal begins in about 1/2 day. No. 316 stainless steel piping or tubing is also satisfactory, but contact time should be limited. Tygon tubing has not been used, but tests indicated that it would be satisfactory. Silver solder and brass are permissible if contact time is limited.

After filling a window it is necessary to stir the solution to eliminate striations caused by density differences. A stainless steel stirrer with collapsible blades has been used. A stirrer with a two to three inch diameter propeller driven with a 1/4 horsepower floor fan motor will produce a clear window in less than five minutes. The stirrer must not introduce air bubbles into the liquid.

The temperature of zinc bromide should not be allowed to fall below 32°F. Slightly below this temperature crystallization will take place. Heating and considerable stirring are necessary to get the crystals back into solution. Instructions in the specifications require that zinc bromide solution be maintained above 32°F. during shipment to the customer.

Glass carboys are completely satisfactory as a shipping container for zinc bromide. Koroseal-lined drums have been used but were discarded because of contamination of the solution with the bleeding plasticizer. Fifty-gallon drums made from 1/4 inch thick steel were lined with Amercoat 31 paint. One shipment has been made in these containers. It was satisfactory except that the gasket partially stripped the paint when the drum was opened. Double gaskets would eliminate the trouble.

The intermixing of various batches of zinc bromide should be avoided. As pointed out in the section "Hazes Formed from Supersaturated Solutions" intermixing may in some cases result in the formation of a sulphate type haze which lowers the contrast of objects being viewed through the window. In no case has a window become unusable because of this haze.

Where intermixing is unavoidable, it is desirable to fill the windows as soon as possible in order to allow time for the haze to settle before the facility is put into use. The settling time may be as long as 9 months; however, the worse the haze, the more rapidly it would settle.

### VIII. MEASUREMENT OF HAZE

The magnitude of the haze with which one is concerned in liquids for viewing windows is such that an objectionable haze in a window would be invisible to the eye in a 20-cubic centimeter sample. A convenient way of qualitatively observing this small amount of haze is to project an image of a projection lamp filament into the sample. In any observation of haze in zinc bromide, it is necessary to allow several hours for air bubbles to rise. Bubbles are always introduced when zinc bromide is poured.

Haze has been measured at the Dow Chemical Company with the General Electric Spectrophotometer. The primary light beam passes through the sample, through an exit hole in the integrating sphere, and into a light trap. Light scattered from the beam by the sample is collected by the integrating sphere and measured. The readings obtained with this instrument are near its limit of sensitivity and are, therefore, not entirely satisfactory.

Measurement on the Coleman Photo-Nephelometer was not satisfactory. Here again the instrument did not have sufficient sensitivity even when the comparison standard was "set up" on the scale to give a 3X increase in sensitivity.

The Fisher Scientific Company Nefluoro-Photometer was found to have more than enough sensitivity. The haze standards for comparison are manufactured by the Coleman Instrument Company for use in their instrument. For measuring zinc bromide in the Fisher instrument, the haze standards were modified as explained in Section IV C of the Appendix. In order to convert haze readings relative to the standard into a number which is proportional to the amount of haze in the zinc bromide, it is necessary to know the background or zero haze reading. In the usual determinations of haze in dilute water solutions, distilled water can be used as a solution of zero haze. If distilled water is assumed to have zero haze and zinc bromide solution is then measured in the same cell, a large negative haze reading will be obtained. In other words, the light scatter due to a difference in refractive index at the water-glass interface of the cell is sufficient to throw the instrument off scale. The obvious solution is to find a liquid with zero haze and an index of refraction the same as zinc bromide. Such a material has not been found.

A sample of zinc bromide with a haze of only 1.4 nephelos units was treated with barium and sulphate in order to increase the particle size of the sulphate haze. The particles were allowed to settle for 3 months. The sample was acidified to remove hydroxide type hazes. The remaining haze was barely visible to the eye with the instrument shutter open and measured 0.75 units. This was the least amount of haze ever observed in any zinc bromide solution.

A selected glass rod was coated in the proper pattern with the same paint used as a backing on the liquid sample cells. To the eye it appeared to be perfectly transparent. Unfortunately, upon observing the rod through the

filter opening of the instrument with a small mirror and with the instrument shutter open; a fine line of microscopic bubbles was observed. The haze reading was 0.7 nephelos units.

From the above two tests, allowing for the bubbles in the glass rod and for Raleigh scattering of the bromine atoms of the zinc bromide, it was concluded that the background reading due to light reflected from the black paint backing of the sample cells and other causes was somewhat less than 0.7, probably 0.3-0.5 units. Neglecting this small amount of background, the haze readings on this instrument are essentially proportional to the haze content of the sample.

A haze standard with a calibrated value of 8 to 10 nephelos units was used as a reference. Instrument sensitivity is then defined by adjusting the sensitivity control to make the standard read 80-100 (10 times calibrated value).

Readings obtained in a zinc bromide sample should then be divided by 10 to obtain nephelos units. Since the nephelos standard is at the low end of the Coleman "nephelos" range, this standard was later replaced with a 40-unit standard and the scattered light attenuated to 4.0 nephelos units with a calibrated neutral density filter. It was believed that this procedure using a higher valued standard attenuated to near the zinc bromide haze specification limit (3.5 "nephelos") would yield more accuracy. In this case the instrument sensitivity is adjusted to make the standard plus filter combination read a value equal to the standard calibration times the filter transmission factor times ten. In other words, with a 40 nephelos standard and a 1.0 neutral density filter the combination should read  $40 \times 0.1 \times 10$  or 40 on the instrument. The zinc bromide sample is read with the filter removed, and the reading obtained is 10 times the nephelos value of the zinc bromide.

It was found that there is some variation in results obtained on the same zinc bromide when various sample cells were used. Deviation from the average for six cells was found to be:

Cell #1	low 0.04	nephelos units
2	low 0.13	nephelos units
3	high 0.05	nephelos units
4	high 0.04	nephelos units
5	high 0.11	nephelos units
6	low 0.04	nephelos units

These deviations have remained constant for many months.

Benzene is a convenient liquid standard for less accurate work. Haze in two samples each of 3 different batches of reagent grade benzene was measured on the material as it came from the bottle.



	<u>Sample 1</u>	<u>Sample 2</u>
Baker and Adamson Lot Go57	2.05	2.08
Lot G110	2.15	2.16
Mallinkrodt Lot YLR-1	2.35	2.35

Haze as measured with the General Electric instrument, Fisher instrument, and as observed in a window are not well correlated. Differences in results with the two instruments may be due to the fact that one measures light scattered at right angles while the other measures low angle scattering. Experience has shown that if a sample meets the haze specification as determined by either instrument for a period of 30 days, it should give satisfactory results when used in a window.

#### IX. MISCELLANEOUS PROPERTIES

The refractive index of materials for shielding windows is of interest because this property permits a greater field of view in a high-index window as compared to the same size window constructed of low-index material. High-index materials also make objects appear closer than they really are. A plot of refractive index for sodium light vs. density of zinc bromide solutions at 25°C. is shown in Figure 5. The temperature coefficient of refractive index is 0.000336/°C.

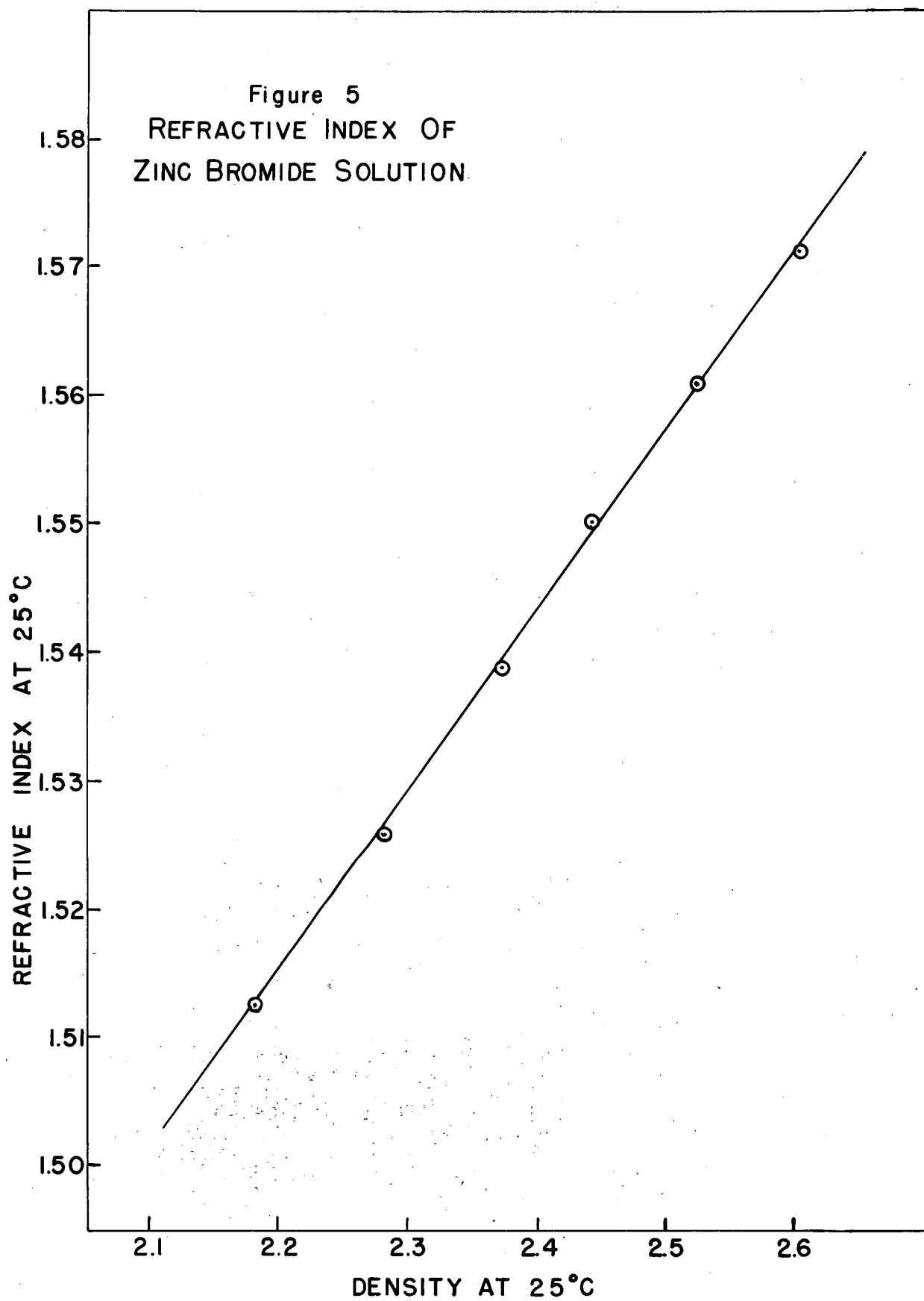
In designing window tanks provision must be made for taking care of the thermal expansion of the liquid. The cubical coefficient of expansion for optical grade zinc bromide is about  $0.6 \times 10^{-3}$  per degree C.

The viscosity at 25°C. is about 7.3 times as great as that of water at the same temperature.

The price of zinc bromide solution is usually computed on a dry weight basis. The composition as stated by the Dow Chemical Company is:

Solution density	2.50,	dry weight zinc bromide 77.0%
Solution density	2.54,	dry weight zinc bromide 78.3%

From the above the dry weight of zinc bromide per gallon of a 2.50 density solution may be computed as  $8.33 \times 2.50 \times 0.770 = 16.03$  pounds per gallon. Assuming the current price of zinc bromide is 78 cents per pound dry weight, the price per pound of zinc bromide solution would be  $78 \times 0.77 = 60.1$  cents.



## X. CONCLUSION

Over the past two years investigation of dense zinc bromide solutions has resulted in the availability of a commercial product for use as a transparent shielding material with the following properties:

1. Transmission for light is superior to "nonbrowning" lime glass.
2. Freedom from optical inhomogeneities which are usually present in thick nonbrowning glass windows.
3. Shielding power for gamma radiation equal to nonbrowning glass or concrete.
4. Capability of withstanding nearly the same total dose of radiation as nonbrowning glass without any noticeable effects. This means a total radiation dose of at least  $10^7$  roentgens or at least 1000 times that permitted in ordinary lime glass.
5. No observable deterioration. After three years of continuous use there has been no observable deterioration. As long as the permissible total radiation dose is not exceeded there is no reason to believe that re-filtration or replacement will be necessary.

6. Low cost. The present cost is approximately one-fourth that of nonbrowning glass or about 60 cents per pound of solution.

There are two undesirable properties of zinc bromide solution, the importance of which depends to a great extent on the type of installation.

1. It is a liquid, therefore there is the danger of suddenly losing the shield if a cover plate were to rupture.
2. Glass is known to be stable over very long periods of time. Since the history of optical grade zinc bromide covers only a few years, one may hesitate to use it in a permanent installation where temporary interruption of viewing for replacement of the solution would be costly.

Specifications are now available for the purchase of optical grade zinc bromide.

In addition to the development of a satisfactory solution, suitable materials for containing and handling zinc bromide have been found. Amercoat 31 paint, tank lining grade Koroseal, or copper welded copper are recommended as window tank linings.

The Dow Chemical Company, Midland, Michigan, is presently the only producer; however, there are three other companies now interested in optical grade zinc bromide manufacture. These are:

Chemo Puro Mfg. Corporation  
41 32nd Place  
Long Island City, New York

J. T. Baker Chemical Company  
Phillipsburg, N. J.

Michigan Chemical Company  
Saint Louis, Michigan

APPENDIXSPECIFICATIONS and REQUIREMENTS FOR  
OPTICAL GRADE ZINC BROMIDE SOLUTION  
JULY 8, 1952I. GENERAL

## A. Containers shall be:

1. Glass, with glass stoppers provided with a dust hood to prevent the accumulation of dust on the lip of the container. This hood may be plastic sheeting tied around the neck of the container.
2. Steel drums of sufficient mechanical strength with securely bolted covers and internally painted with seven coats of Amercoat, System 31, black paint (prime, three body, and three seal coats over a sand-blasted surface). Two gaskets made of grade 116 Koro-seal should be used since these gaskets adhere to the paint but not to each other.

B. The purchaser is to be supplied with a one-pint composite sample representing the entire shipment. If the manufacturer is requested to add hydroxylamine stabilizer, this sample shall be collected before the addition of the stabilizer. The sample shall meet all of the specifications for a period of 30 days after it leaves the supplier's plant. In the event that it does not, the material which it represents will be reprocessed by the supplier at no cost to the purchaser.

C. The solution shall be maintained above 32°F. at all times.

II. PHYSICAL PROPERTIES

A. The density of the solution shall be not less than 2.50 grams per milliliter nor more than 2.54 grams per milliliter.

B.\* The transmission of light of wavelength 5890 angstrom units through a 5-centimeter path of solution shall be at least 97% of that of an equal path length of water.

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\*All light transmission measurements must be made in silica window cells with no correction applied for loss of light at the window surfaces.

C.\* The luminous transmission for solar light (ICI illuminant "C") for a 5-centimeter path length shall be not less than 96% of that of an equal path length of water.

ALTERNATE: (B) AND (C)

The transmission for light of 5500 angstrom units wavelength through a 5-centimeter path of solution shall be at least 96% of that of an equal path length of water.

The yellowness shall be less than 20. Yellowness is defined as transmission at 6500 angstroms minus transmission at 4500 angstroms divided by transmission at 5500 angstroms, all times 100.

D. Haze shall be less than 3.5 nephelos units as determined with the Fisher Scientific Company Nefluoro-Photometer using the method described in Appendix, Section IV C.

ALTERNATE: (D)

The haze as measured on the General Electric Recording Spectrophotometer according to the ASTM method designated as D10003-49T, page 666, part 6, shall be less than 0.5%. Precaution should be taken to insure that dust particles on the zinc bromide-containing cell window do not introduce large errors.

III. CHEMICAL PROPERTIES

A. The solution shall be essentially a pure zinc bromide solution in water.

B. Alkalinity shall be not less than 8 milliliter nor more than 16 milliliter.

C. The iron content shall be less than 50 parts per million.

D. The solution shall be completely oxidized during manufacture to insure the absence of the sulphide ion.

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\*All light transmission measurements must be made in silica window cells with no correction applied for loss of light at the window surfaces.

#### IV. SPECIAL METHODS FOR TESTING

A. The transmission of light of wavelength 5890 angstrom units can be determined with the Beckman Model DU or General Electric Spectrophotometer or other instruments of comparable accuracy.

B. Luminous transmission for solar light may be determined by an appropriate calculation from data obtained with a Beckman Model DU Spectrophotometer, General Electric Recording Spectrophotometer, or other instrument of comparable accuracy. The calculation can be performed as indicated on page 51, Handbook of Colorimetry, by A. C. Hardy.

Any other instrument of comparable accuracy may be used if the light source has the spectral quality of solar light (ICI illuminant "C") and the detecting element a spectral sensitivity essentially that of the human eye.

C. Haze is measured with a Fisher Scientific Company Nefluorophotometer with certain modifications.

The black coating on the sample cells supplied with the instrument is removed with the aid of hydrochloric acid. The cells are then immersed in undiluted "Duco" black lacquer #246-2048 and allowed to dry 3-5 hours. Part of the coating is shaved off with a razor blade so that the cells are now coated in the original pattern. This recoating procedure is necessary because the original coating is attacked by zinc bromide and gives erroneous results. The instrument is used with the slit removed, a 430 plus filter in the center, a diffuser for the right filter, and the left filter is blank. Position "C" is empty and taped over to prevent dust from falling into it. It was not necessary to put a scatterer in position "A" since the black walls scattered enough light to balance the instrument; however, this may not be the case with other instruments. This position was also taped over to keep out dust. Samples and standards were put into position "B." It was found that the 0% of the dial scale did not correspond to the crossed condition of the polaroids. This was corrected by marking a new index even though at the other end of the scale this did not cause correspondence of the 100% mark with the maximum transmission of the polaroids.

Standards used were the "nephelos haze standards" manufactured by the Coleman Instrument Company modified by coating with black Duco lacquer in the same manner as were the sample cells. A collar is provided to maintain the standard at the proper depth in the instrument.

A wratten neutral density filter or preferably a neutral glass filter with a density of about 1.0 is calibrated on a Beckman Spectrophotometer at the wavelengths of the mercury green, yellow, and blue lines. The density of the filter is then the numerical average of these three readings. A Coleman standard of about 40 nephelos units is coated and provided with a collar as above.

In use, the filter is put in the left filter position and the dial scale set at 10 times the transmission factor of the filter times the calibration value of the standard. The null control is balanced, and the filter removed. The sample is measured, and the readings obtained are "nephelos" times 10. It is necessary that the zinc bromide stand in the measuring cells for four hours before reading to allow air bubbles to rise. These may be seen by viewing down into the cells with the instrument shutter open.

D. Alkalinity is determined by weighing a ten-gram sample, adding 100 cubic centimeters of water, and titrating to a pink end point with tenth normal hydrochloric acid. Methyl red is used in the indicator. The value of the alkalinity is equal to the number of cubic centimeters of acid required.

E. Hydroxylamine hydrochloride content of the solution is determined by titrating the concentrated zinc bromide solution with a ferric iron solution in concentrated zinc bromide.

Iron Solution - add 200 parts per million of iron as ferric chloride to optical grade zinc bromide solution. Add 37% hydrochloric acid until the orange color changes to red (zero alkalinity); now add 1% by volume of HCl in excess. Standardize with a known weight of hydroxylamine hydrochloride in 10 milliliter of zinc bromide. A blank determination should be made to account for other reducing agents present in the 10 milliliter of zinc bromide used for standardization.

Add one milliliter of 37% hydrochloric acid to a 10-milliliter sample of zinc bromide. Heat to near boiling (100°C is satisfactory), and titrate with the iron solution. The end point is a yellow color which is not bleached in 20 minutes when the sample is maintained at 100°C.

The reaction is slow, particularly near the end point; hence sufficient time must be allowed between each addition of iron solution. Prolonged heating results in some oxidation by atmospheric oxygen, but this is only slight over a period of an hour or so.

#### V. ADDITION OF HYDROXYLAMINE STABILIZER WHEN SO REQUESTED BY THE PURCHASER.

Reagent grade hydroxylamine hydrochloride is added at the rate of 4 ounces per 100 gallons of optical grade zinc bromide solution. This may be conveniently done by dissolving the hydroxylamine hydrochloride in about four times its weight of zinc bromide solution. This strong solution may be filtered through a sintered glass funnel if an appreciable amount of haze is present. The proper amount of the strong solution is then added to the main batch of zinc bromide.