FOREWORD

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

This report covers work conducted from 1 February 1961 to 31 December 1961.

The preparation of samples and the evaluation of optical properties were performed by Robert C. Langley, research director, by David B. Kellam, research chemist, and by Edith Verlezza, technician.

Spectrophotometer measurements were made in the research laboratory of the Hanovia Lamp Division of the Engelhard-Hanovia Company. This part of the work was performed by Mr. Bernard Burda, physicist, under the supervision of Dr. Robert Heine-Geldern, director of research.

ABSTRACT

This research was limited to an evaluation of the optical properties of thin films on glass. These films were obtained by the application of metallo-organic solutions of the metals, followed by thermal decomposition of the organics in air.

More than 1000 samples were made. Of these about 329 were measured for percent reflection, percent transmission, or both. It was found that a thin film containing gold, bismuth, barium, silicon, rhodium and chromium has optical properties which meet the minimum goal of this project, namely, absorption of solar energy of wavelengths below 1.5 microns and reflection of wavelengths above 1.5 microns. This system was extensively reformulated without great optical improvement.
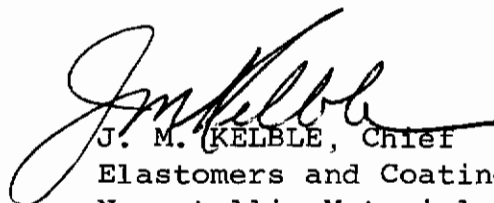
While the research demonstrated that the desired optical properties can be obtained by a single application of the proper solution of gold and other metals, it is noteworthy that the best optical film found was a relatively impure gold film. In this film, minor changes in bismuth, barium, silicon or chromium content had pronounced optical effects.

In the six component system found to be best optically, it was demonstrated that additions of barium or silicon in small amounts or of platinum or palladium in substantial amounts decrease reflection. It was also found that very small chromium additions increase reflection.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:

J. M. KELBLE, Chief
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iii

TABLE OF CONTENTS

LIST OF TABLES

I INTRODUCTION

The goal of this research is to obtain a coating capable of continuous operation at 250° C or higher in a high vacuum (space) environment. This coating is to be formed by thermal decomposition of metallo-organic solutions or suspensions and is to have these optical properties:

(1) High absorption of solar energy of wavelengths shorter than 1.5 microns and high reflection above 1.5 microns, or

(2) High transmission below 1.5 microns and high reflection above 1.5 microns, or

(3) Any combination of the aforementioned properties.

Quantitatively the tentative optical goals were expressed as:

(1) Maximum absorptance of 0.8 to 0.9 below 1.5 microns and reflectance of 0.95 above 1.5 microns.

(2) Transmittance of 0.5 below 1.5 microns and reflectance of 0.9 above this wavelength.

(3) Any combination of transmittance and absorptance to utilize solar radiation of less than 1.5 microns selectively.

Because suspensions have inherent shortcomings when films of optical quality are required, we decided at the outset to concentrate our efforts on solutions of metallo-organic compounds. These solutions permit considerable freedom in the choice of resins, solvents and plasticizers which may be used to obtain precise properties of viscosity, flow and drying time.

Glass was chosen as the substrate material as a matter of convenience. Although glass is not a preferred material for most aerospace applications, it was assumed that a successful optical coating fired on glass at 600° C would have utility on most substrates capable of withstanding this temperature.

As a rapid method of applying various solutions to flat glass,

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1

a spinning technique was used. By dropping an excess amount of a properly formulated solution on to flat soda-lime glass which is spinning at 1550 r.p.m., we were able to obtain reproducible films which are free of the optical defects sometimes encountered in other application techniques. It was found during the production of over 1000 samples by this method, that the best solution for spinning is almost identical in physical properties to a good brushing formulation, i.e., it has moderately fast drying solvents, good secondary flow and a viscosity of one poise or slightly less. Not much has been published on formulating techniques in the field of metallo-organic solutions and most commercial products are supplied to the user as proprietary formulations on the part of the manufacturer. A comprehensive discussion of this formulating art can be found in Fitch(1).

To obtain an organic gold compound with good solubility in organic solvents, it is necessary that the starting organic material be carefully chosen. Ballard(2) describes gold mercaptides made from alpha-pinene mercaptan, beta-pinene mercaptan, dipentene mercaptan, terpinolene mercaptan, menthene mercaptan, alpha-terpineol mercaptan and camphene mercaptan. These mercaptans can be prepared by hydrogenating a sulfurized terpene compound in the presence of a sulfactive hydrogenation catalyst(3). Mercaptans of this type can also be made by the catalytic addition of hydrogen sulfide to cyclic terpenes (4).

Morgan(5) describes the sulfurization of beta-terpineol by heating with elemental sulfur at 165° C. From this terpineol sulfide, a useful organic gold compound can be made by reaction at room temperature with potassium gold chloride dissolved in alcohol.

Organic gold compounds made by these methods are referred to as gold resinates or gold sulforesinates. Compounds of platinum, palladium and rhodium can be made from similar starting materials. Chemnitius(6) describes a platinum resinate prepared by the reaction of a platinum salt with sulfurized turpentine.

"Liquid Bright Gold" is a solution of a gold sulforesinate, rhodium sulforesinate and of several base metals such as bismuth, chromium or vanadium. These metals are organic soluble when in the form of carboxylates. These can be readily made with rosin as the starting material. Morgan(5) describes the reaction of bismuth subnitrate with rosin. The base metal carboxylates are commonly referred to as resinates, e.g., bismuth resinate. Ballard(2) mentions another meth-

2

od of preparing bismuth in organic-soluble form. This is achieved by
the reaction of bismuth trichloride with ethylene chlorohydrin.

No formal literature search was made in connection with this work
but the staff of this laboratory has always kept current in the ce-
ramic, chemical and patent literature, particularly of the precious
metals. The state of the art as presented at the Dayton conference(7)
of November 1960 was studied. Several other publications have some
pertinence. Harris and Fowler(8) have measured the absorption of gold
in the far infrared. Kumar(9) has measured the absorption of glasses
containing these ions: V^3, Cr^3, Mn^3, Fe^2, Co^2, Ni^2 and Cu^2. Colbert
and Morgan(10) have developed an electrically conductive film of gold
which transmits 70% of visible light. Lawson(11) discusses theories
of infrared absorption by inorganic materials.

It was known at the start of this research that thin films ob-
tained by the thermal decomposition of some "Liquid Bright Golds,
Platinums or Palladiums" are fairly efficient reflectors of infrared.
No direct method is known for measuring the thickness of these films,
but in the case of gold the film is nominally 1250 Angstroms (.000005
inches), assuming that the specific gravity of the gold in the film
is the same as that of the bulk metal. At atmospheric pressure, these
films can operate continuously on glass at temperatures as high as
600° C, and on higher temperature substrates such as fused silica,
these films are used commercially at temperatures in the range of 800
-900° C. While the behavior of these films in a vacuum is not known
experimentally, films of bright platinum have been used successfully
in vacuum tubes to conduct electricity.

A proprietary formulation, Liquid Bright White Gold #10, is a
better infrared reflector than a polished aluminum standard, but also
reflects highly in the visible. Another formulation, Liquid Bright
Palladium #62, has visible reflection which meets the minimum goal
of this work, but reflects poorly in the infrared. These values are
listed in Table 1.

One approach considered was the application of several coats,
fired individually, to attempt to obtain the selective antireflection
possible with vacuum deposited films of closely controlled thickness.
A second approach was that of adding novel base metals to "Liquid
Bright" solutions to obtain the desired optical result with a single
application and a single firing. This second method was considered
to be the more practical one, so it was stressed. Encouraging results
were obtained early in the investigation so the multiple coating meth-
od was abandoned.

II EXPERIMENTAL

To assemble as much preliminary information as possible, organic solutions were made of all of the elements which can be used as additives to organic precious metal solutions. These elements are made soluble in organic solvents by first making the proper carboxylate, alcoholate or mercaptide. The starting acid, alcohol or mercaptan is chosen to give high solubility of the element, low volatility, complete decomposition of the organics upon heating, and compatibility with solutions of other metals. Fitch(1) describes how a number of gold mercaptides are made.

Including the precious metals, 47 solutions of single elements were made. Very few of the solutions had the proper viscosity, surface tension, or drying rate to apply well by the spinning technique. In some cases, solutions which did apply well blistered during firing. This defect could usually be traced to too high concentration of the element in solution. Formulation of the solutions to obtain fired films free of crazing or blistering proceeded well once it had been determined that a solution of about one poise containing moderately fast drying solvents gave the best wet application. This formulation involved dilution with aromatic solvents and essential oils and the addition of solutions of asphalt, rosin, sulfurized rosin, etc., to aid in film formation.

Two inch squares of soda-lime glass one-sixteenth inch thick were washed with a detergent solution in a household type dishwashing machine. The glass was allowed to dry in the machine and was not handled on the surface to be decorated. The spinning machine was housed in a dust-free cabinet in which a positive pressure was maintained by blowing in air through a filter. The glass was placed flat in the machine and dusted lightly with a camel's hair brush. The solution to be applied was dropped on to the approximate center of the glass while it was spinning at 1550 r.p.m. For a properly formulated solution, application was simple and rapid. It was necessary only to observe that an excess of solution was used. The glass was kept spinning until no more solution was flung from the edges. The glass was removed from the spinning device and kept in the dust-free cabinet to prevent airborne dust from marring the still tacky film. When a number of samples had been coated, they were carried, under cover, to an electrically heated continuous lehr. They were placed on flat refractory supports and fired in air to a peak temperature of 600° C. The total

4

lehr cycle was 1.5 hours with the glass maintained at peak tempera-
ture for 10 minutes.

Under the firing conditions used, all of the elements which form
oxides presumably form their highest stable oxides. These may then
in turn react with the glass substrate. In the case of gold and plat-
inum, specular films develop at 300 to 400° C, but fail between this
temperature and 600° C. This failure takes the form of loss of mirror
and loss of electrical conductivity. Under magnification the formerly
smooth films have broken down to discrete areas of metal. It is well
known in the art that this failure can be eliminated by the addition
of small amounts of rhodium to gold or platinum and all of the "Liquid
Bright Gold" and "Liquid Bright Platinum" of commerce do contain rho-
dium.

The 47 single elements from which films were formed are:

Silver	Aluminum	Cadmium	Lanthanum
Platinum	Lithium	Tin	Magnesium
Gold	Potassium	Antimony	Tungsten
Palladium	Yttrium	Barium	Germanium
Rhodium	Chromium	Gallium	Copper
Ruthenium	Manganese	Neodymium	Rhenium
Iridium	Iron	Praeseodymium	Uranium
Boron	Nickel	Niobium	Molybdenum
Cobalt	Zinc	Cerium	Indium
Silicon	Tantalum	Lead	Phosphorus
Calcium	Strontium	Bismuth	Sodium
Vanadium	Zirconium	Titanium	

Still as a preliminary step, it was decided to make a number of
solutions containing two or more elements. These were readily made
since all of the metallo-organic solutions used are mutually miscible.
Typical solutions from which films were obtained are:

Gold-silver
Silver-niobium
Silver-palladium
Silicon-bismuth
Bismuth-chromium
Bismuth-tin
Bismuth-chromium-tin

5

Bismuth-chromium-silicon
Bismuth-barium-silicon
Bismuth-cobalt-titanium
Vanadium-chromium
Silicon-tin-iron-nickel
Antimony-vanadium-chromium-bismuth
Boron-silicon-calcium-titanium-zinc-tin
Bismuth-cobalt-chromium-titanium
Silicon-iron-bismuth-nickel
Lead-aluminum-silicon-boron
Silicon-cobalt-bismuth-titanium
Platinum-lithium
Palladium-vanadium
Gold-titanium-vanadium-chromium-bismuth
Gold-iron-vanadium-chromium-bismuth

   To some of the solutions of single elements and to all of the
above solutions of multiple elements, gold and rhodium were added.
The approach was frankly empirical and necessarily highly random be-
cause of the infinite number of solutions possible with multiple ele-
ments. A total of 149 solutions was made, applied and fired as above,
and measured for percent transmission of film plus glass in air over
the range of 0.4 to 2.0 microns. A Beckman DU instrument was used
and only transmission was measured in this preliminary screening.
Films which transmitted higher than 45% at 1.5 microns were not meas-
ured further.

   None of the 47 films obtained from single elements was metallic,
i.e., all were non-conductive. Only the films formed from cobalt,
calcium, manganese, iron, copper, uranium and palladium showed enough
of a decrease in transmission at 1.5 microns to warrant reflection
measurements. These values are listed in Table 2. Specular reflec-
tion of these in terms of percent reflection of a plane, polished alu-
minum mirror was measured over the range 0.4 to 4.0 microns on a Per-
kin-Elmer Model 83 monochromator. Table 3 gives these values. All
reflected poorly over the entire range.

   Out of the 102 films containing more than one element, 29 had
low transmission at 1.5 microns. All of these contained gold, gold-
platinum, or gold-palladium as the principal ingredients. These re-
sults tended to confirm our assumption that the goals of this work
could be met by adding one or more base metals to otherwise conven-

6

tional precious metal formulations. These 29 samples were then measured for percent reflection and one of the films gave values which meet the minimum optical goal. These results are listed in Table 4.

This promising solution was identified as Trial #94 and contained the following.

Weight % in solution		Weight % in fired film
8.630	Au	89.5
.039	Rh	.4
.430	Bi_2O_3	4.5
.020	Cr_2O_3	.2
.167	SiO_2	1.7
.360	BaO	3.7
9.646	total	100.0

The fired film of #94 differs from conventional bright gold films in that it is less pure; most of the ceramic bright golds in common use contain about 95% Au in the fired film. Trial #94 also differs in that it contains substantial amounts of barium and silicon, elements not ordinarily used in bright golds. Trial #94 resembles other bright golds in that the film on glass is highly specular and is electrically conductive, i.e., it is metallic.

Within fairly broad limits, a solution such as #94 can be reformulated to vary the ratio of one component to the others in the solution and thus in the fired film. The metallo-organic compounds of the six components are mutually miscible in any proportions and a large number of variations can be made simply by weighing off the proper amounts of the solutions involved. Because of this and because the spinning technique permits rapid production of a large number of fired samples, 85 variations of #94 were made. All were measured for percent reflection over the range of 0.4 to 4.0 microns.

To determine the effect of film thickness, we made solutions containing the same proportions as #94 but at 4.8 and at 14.5 weight percent in solution. Since these solutions had the same viscosity as #94, films obtained from them should be one-half as thick and 1.5 times the thickness of film #94 respectively. The thin film reflected much less than #94 in both the visible and infra-red. The thicker film was a slight improvement over #94 in that it was a better reflector from

3.0 to 4.0 microns. It also reflected slightly less at 0.5 microns, so this trial, #165, can be considered as slightly better than #94 overall. Table 5 gives the comparison of these two trials with #94.

Keeping the gold and rhodium of #94 constant, the oxide formers (bismuth, barium, silicon and chromium) were increased as a group to double and triple their concentration in #94. These trials gave curves with much lower reflection below 1.5 microns but at the sacrifice of sharply lowered reflection above 1.5 microns. See Table 6. These trials high in oxide formers gave films which were non-metallic, i.e., they were not electrically conductive. Since these films have the same amount of gold per unit area as the film of #94, it suggests that gold must be in the metallic form to reflect infra-red well.

With gold and rhodium constant, the four base metals of #94 were increased singly to double their original concentration. These changes had pronounced optical effects and this was somewhat unexpected in view of their small concentrations in the film in relation to gold. Doubled barium or silicon caused decreased reflection both below and above 1.5 microns. Doubled bismuth caused increased reflection below 1.5 microns without much effect above 1.5 microns. Increased chromium caused increased reflection generally. Considering that chromium is present in the fired film of #94 only to the extent of 0.2% calculated as Cr_2O_3, it is very interesting that the rather subtle change to double this concentration has such a pronounced optical effect. Table 7 lists these four trials.

Effect of Platinum and Palladium Substitutions for Gold

The film formed from a conventional formulation such as Liquid Bright Palladium #62 (see Table 1) contains 1.5 parts palladium to 4.5 parts gold and has much lower reflection in the visible range than a conventional Liquid Bright Gold film. Four series were run with 10 and 20% platinum and palladium substituted for gold in the four trials listed in Table 7. In all sixteen samples in these four series, substitution of either 10 or 20% of either platinum or palladium resulted in lower reflection than that of Trial #94 above 1.5 microns.

In the series equivalent to #94 with barium doubled, all four substitutions of platinum and palladium resulted in lower reflection than #94 below 1.5 microns.

8

In the series equivalent to #94 with silicon doubled, all four substitutions of platinum and palladium resulted in lower reflection than #94 below 1.5 microns.

In the two series equivalent to #94 with bismuth doubled and to #94 with chromium doubled, 10% substitutions of either platinum or palladium did not result in reflection as low as #94 below 1.5 microns. Platinum or palladium substitutions of 20% in these two series, however, resulted in lower reflection than #94 below 1.5 microns.

Table 8 gives the comparison among trials #94, #94 with bismuth doubled, #94 with bismuth doubled and 10% of the gold replaced by palladium, and #94 with bismuth doubled and 20% of the gold replaced by palladium. These results are typical of the platinum and palladium substitution series; either metal in the proper amount does lower the reflection below 1.5 microns of any of the trials of Table 7, but reflection above 1.5 microns is decreased too.

Effect of Further Chromium Increases

Since the relatively minor increase to double the original concentration in trial #94 had such a pronounced optical effect, samples were made containing four, six and eight times the chromium content of #94. Table 9 lists the specular reflection of these samples. All were electrically conductive, i.e., metallic.

Effect of Platinum and Palladium Substitutions Plus Increased Chromium

To the trials containing four, six and eight times the chromium content of trial #94, 10 and 20% substitutions of platinum and palladium for gold were made. Table 10 lists the results obtained with platinum substitutions. Results with palladium substitutions are similar.

Investigation of a Second Organic Gold Compound

Throughout the experimental work, the solutions were made using gold in the form of gold sulforesinate. This compound is a standard one but it has some limitations. The highest concentration of gold obtainable in a low viscosity solution is 24% and the minimum firing

temperature at which the organic compound decomposes to give a metallic film is 250° C. To make the best solution for optical purposes as versatile as possible, some trials were made to investigate the replacement of this gold compound with gold tertiary dodecyl mercaptide. GTDM has the advantage that fluid solutions containing as high as 35% Au can be made, but more importantly, GTDM decomposes to a metallic film at 150° C. This lower firing temperature makes solutions containing GTDM more desirable in that films formed from them can be obtained on relatively low temperature substrates (e.g., epoxy, silicone and polyester plastics). On refractory substrates, the upper temperature limit of films obtained from GTDM is the same as that of those obtained from gold sulforesinate solutions, i.e., about 900° C.

With this in mind, trial #94 was reformulated using GTDM in place of gold sulforesinate, and varying total content, proportion of base to precious metal and base metals individually. The platinum and palladium series described above were also repeated using GTDM. Examination of reflection data indicates that formulations containing either gold compound give similar curves provided that solution viscosity is adjusted to give the same wet application and thus the same fired film thickness.

Application by Brushing and Spraying

The spinning technique is a handy method for coating large numbers of samples for laboratory purposes but a more practical application method is needed when objects of complex shape or large size must be coated. A few trials were made by brushing Solutions #94 and #165 on flat glass. These were measured for specular reflection from 0.3 to 15.0 microns. A Perkin-Elmer Model 83 monochromator was used from 0.3 to 2.5 microns, and a Perkin-Elmer Infracord was used from 2.5 to 15.0 microns. The samples were also measured on a Beckman DU spectrophotometer for transmission from 0.4 to 2.0 microns. Tables 11 and 12 give these values. These values differ significantly from those obtained on the samples made by the spinning technique. This indicates that some method of controlling the brushing application is necessary.

Test Methods

In a rough test of resistance to elevated temperatures, trial #94 was sprayed on a glazed ceramic and fired to 740° C with a ten minute soak at this temperature. No apparent change occurred in the film and it was still electrically conductive. The sample was not heated to destruction, since the failure of thin precious metal films

depends to a considerable extent on the substrate.

To test adherence of films #94 and #165 on glass, the "Scotch Tape" test was used. There was no removal of gold in either case. This is not considered a severe test for the bright golds used commercially on glass and ceramic glazes. The adherence of thin gold films to most substrates depends on the base metal content of the precious metal formulation, the chemical composition of the substrate, and the time and temperature of the firing cycle. Belser(12) has established some relation between the "Scotch Tape" test and a quantitative test method.

During the experimental work, it was not necessary to clean the samples after firing and they were handled carefully at the edges in packaging and when placed in the spectrophotometer. Oily residue from fingerprints was noticed in a few cases; this was readily removed by wiping with a cloth wet with ethyl acetate and there was no damage to the film.

All of the fired films were tested for electrical conductivity using a Weston Model 564 battery powered ohmmeter. With the pointed probes one inch apart, those gold films described as conductive had resistances of less than 10 ohms. Films described as non-conductive gave values in excess of 200,000 ohms so this distinction is clear-cut.

Specular reflection of the samples is expressed in terms of a plane, polished aluminum first surface mirror supplied by Perkin-Elmer Corporation. This mirror has reflectivity of 90 to 92% between 0.4 and 0.8 microns. From 0.8 to 0.9 microns, the reflectivity is 89% or higher. Between 0.9 and 4.0 microns, the reflectivity increases steadily to a value of 97% at 4.0 microns. No numerical values at wavelengths longer than 4.0 microns are available, but the supplier states that reflectivity is high.

In this investigation, only specular reflection was measured. Some standard bright gold and bright platinum films measured during this work gave specular values which compare quite closely to values for total reflection on the same films obtained in earlier work, so it is considered that diffuse reflection is negligible. Figures 1 and 2 show calculated values for percent absorption of trials #94 and #165. These approximate values were obtained by subtracting percent

11

specular reflection plus transmission from unity.

Organic Constituents of Test Solutions

Tables 13 and 14 give details of the organic components of trial solutions #94 and #165. These solutions were formulated to have viscosities of slightly less than one poise, measured on a Brookfield Viscometer. The volatile solvents were chosen to give moderately fast drying films.

Solutions of each of the metals contained in trials #94 and #165 are commercially available from Engelhard Industries or they can be made by the methods described in Ballard(2) and Morgan(5).

III DISCUSSION

The experimental work demonstrates the ease with which thin films
of single metals or of complex mixtures of metals can be obtained from
metallo-organic solutions by firing in air. The mixing of solutions
takes very little time and the spinning method of application allows
peak production of about 25 samples per hour. Firing in a continuous
lehr is largely automatic. During the course of the work, a much
greater amount of time was devoted to the planning of trials and to
the evaluation of spectrophotometer data than to the actual production
of samples.

While only small specimens were coated in this work, metallo-
organic solutions have the inherent advantage that they can be formu-
lated for application by practical techniques to objects of complex
shape or large size. This application technique also has an advantage
over vacuum deposition or electroplating in that a number of metals
can be applied to a substrate simultaneously. Obtaining a homogeneous
film of a six component system such as trial #94 by vacuum deposition
would be a formidable task.

The fact that films obtained by brush application give signifi-
cantly different reflection than films applied by the spinning tech-
nique presents an obstacle, though not an insurmountable one. As
shown in Table 5, there is a range in fired film thickness where re-
flection is fairly constant. Trial #165 is nominally 50% thicker than
trial #94 but reflection of the two films is quite similar. The four
results of trial #165 listed in Table 11 have fairly good consistency
considering that no pains were taken to control wet application close-
ly. A method of doing this exists. The solution can be colored by
dissolving an organic dye in it and the wet application can be checked
against a standard application by measuring either color intensity or
light transmission using a suitable device.

The work turned up two areas of novelty. The theory usually
cited about metals which are good infrared reflectors states that
these metals (aluminum, copper, silver and gold) must be fairly pure
and free of oxides or alloying metals. This investigation has shown
that the infrared reflection of pure aluminum can be matched very
closely by a gold film which has substantial amounts of base metal
oxides uniformly distributed throughout the gold.

13

The second interesting fact is that minor changes in the base metals of the best optical film have such pronounced optical effects. Table 7 and Table 9 list results which suggest that wide changes in the optical properties of a gold film should be possible with the proper combination of these or other oxide formers in small amounts.

Once an optical film had been found which was useful for the present purposes, it proved quite easy to decrease its reflection below 1.5 microns. This could be done by the addition of small amounts of barium or silicon or by the substitution of substantial amounts of either platinum or palladium for part of the gold. All such changes, however, resulted in some sacrifice of reflection above 1.5 microns. Although 85 variations of the best film found did not result in any great improvement, this number of trials barely scratches the surface of the very large number of variations possible in the multi-component system.

IV   CONCLUSIONS

Specular gold films about 1250 Angstroms thick, can be readily obtained on glass by thermal decomposition in air of a solution of a gold organic compound.

A particular gold film, only 89.5% Au by weight, containing rhodium and oxides of bismuth, barium, chromium, and silicon, reflects as well as pure aluminum in the range of 1.5 to 15 microns. This film absorbs enough energy of wavelengths shorter than 1.5 microns to be potentially useful for some solar energy purposes; and thus satisfies the minimum goal of this contract.

The film of gold, rhodium, bismuth, barium, chromium and silicon can be changed optically by small changes in content of the four oxide formers. Increased barium or silicon decrease reflection. Increased chromium in very small amounts increases reflection.

When substantial amounts of platinum or palladium are substituted for gold in the film of gold, rhodium, bismuth, barium, chromium and silicon, reflection both below and above 1.5 microns is decreased.

15

V   FUTURE PROGRAM

No further work is planned toward improving the optical proper-
ties of the best film found in this investigation. During 1962 an
effort will be made to apply by some practical means (brushing or
spraying) Solutions #94 and #165 to a substrate which has utility in
high temperature space applications. Using Inconel as the substrate,
various diffusion barriers will be applied by flame spraying or ceram-
ic techniques. The optical coating developed in this work will be
applied to the diffusion barrier with the intention of finding a dif-
fusion barrier which will not cause the optical film to deteriorate
when operated at 800° C in a vacuum equivalent to that found in space.

16

Table 1

Reflection below 0.8 microns compared to magnesium carbonate.
Above 0.8 microns in terms of a plane, polished aluminum mirror.

Wavelength in microns	% R White Gold #10	% R Palladium #62
0.4	38	26
0.5	47	27
0.6	64	24
0.7	75	26
0.8	84	29
0.9	92	30
1.0	94	30
1.1	96	31
1.2	97	33
1.3	98	36
1.4	98	39
1.5	99	43
1.6	100	46
1.7	101	49
1.8	101	51
1.9	102	53
2.0	102	56

Table 1:   REFLECTION OF BRIGHT WHITE GOLD #10 AND BRIGHT PALLADIUM #62

17

Table 2

Transmission of film and glass in air.

Wavelength in microns	Blank Glass	Glass plus						
		Co	Ca	Mn	Fe	Cu	U	Pd
0.4	91.3	1.9	16.0	9.0	1.1	3.4	13.6	15.0
0.5	92.0	5.6	30.0	18.7	12.0	9.6	35.2	19.6
0.6	91.6	21.0	41.6	32.8	52.0	23.4	60.6	40.0
0.7	91.0	28.0	51.6	48.0	77.6	46.0	69.4	51.0
0.8	90.4	33.3	58.6	57.5	84.0	69.0	65.3	57.6
0.9	89.7	72.0	64.0	65.4	81.2	79.8	61.3	62.3
1.0	89.5	80.0	68.0	71.0	78.3	82.0	58.7	66.3
1.1	89.8	76.6	70.6	73.6	76.3	83.2	58.6	69.3
1.2	89.4	65.5	71.6	74.6	74.3	82.7	59.3	77.6
1.3	89.6	58.0	72.4	73.0	72.4	81.0	59.7	71.6
1.4	89.3	48.7	59.7	58.5	61.3	66.6	51.4	60.0
1.5	89.5	36.3	43.4	40.0	43.8	45.0	37.4	41.6
1.6	89.5	27.0	34.4	29.4	32.4	32.6	29.6	32.6
1.8	90.4	16.4	26.8	21.0	19.5	19.8	23.6	24.5
1.9	90.7							
2.0	91.0	10.5	25.0	19.3	12.4	14.0	24.3	21.0

Table 2:   TRANSMISSION OF FILMS FORMED FROM SOLUTIONS OF SINGLE METALS

18

Table 3

Specular reflection in terms of a plane, polished aluminum mirror.

Wavelength in microns	% R					
	Co	Mn	Fe	Cu	U	Pd
0.4	12	12	14	12	14	17
0.5	9	10	13	5	11	20
0.6	8	11	16	3	6	25
0.8	12	9	6	3	6	25
1.0	6	11	11	6	8	25
1.2	9	14	14	9	10	19
1.4	16	16	17	9	10	15
1.6	22	17	17	9	10	13
1.8	22	15	17	9	10	11
2.0	21	14	16	9	10	10
2.2	20	13	15	8	9	10
2.4	19	12	15	8	7	9
2.6	19	11	15	8	7	8
2.8	17	9	12	7	6	6
3.0	12	8	10	5	4	5
3.2	14	7	10	5	4	5
3.4	14	7	11	5	3	5
3.6	7	7	9	6	3	4
3.8	12	6	9	5	3	6
4.0	10	5	7	6	1	5

Note: The film of Ca measured for transmission (Table 2) had no specular reflection.

Table 3: REFLECTION OF FILMS FORMED FROM SOLUTIONS OF SINGLE METALS

Table 4

Specular reflection in terms of a plane,'polished aluminum mirror. Transmission is that of the film plus glass in air.

Wavelength in microns	% R	% T
0.4	57.0	2.0
0.5	31.0	4.2
0.6	33.7	1.6
0.8	52.2	1.7
1.0	61.2	1.7
1.2	72.7	1.4
1.4	82.0	1.4
1.6	96.0	1.6
1.8	96.7	1.7
2.0	96.6	2.1
2.2	95.5	
2.4	95.0	
2.6	97.8	
2.8	94.5	
3.0	81.7	
3.2	81.0	
3.4	91.8	
3.6	91.6	
3.8	87.2	
4.0	84.2	

Figuring absorption by difference, it is interesting to note that #94 absorbs heavily at 0.5 microns, where solar radiation peaks.

Table 4: REFLECTION AND TRANSMISSION OF TRIAL #94

Table 5

Specular reflection in terms of a plane, polished aluminum mirror.

Wavelength in microns	#94	Trial Number	
		#164 (.5 #94)	#165 (1.5 #94)
0.4	57.0	22.9	55.6
0.5	31.0	19.6	29.4
0.6	33.7	31.2	47.5
0.8	52.2	31.2	49.2
1.0	61.2	30.9	63.3
1.2	72.7	32.4	74.7
1.4	82.0	35.2	86.0
1.6	96.0	35.8	88.5
1.8	96.7	37.9	89.2
2.0	96.6	39.8	91.8
2.2	95.5	41.7	93.5
2.4	95.0	41.8	93.8
2.6	97.8	45.0	97.0
2.8	94.5	44.3	90.0
3.0	81.7	45.0	93.0
3.2	81.0	45.8	94.5
3.4	91.8	43.4	90.8
3.6	91.6	44.8	95.6
3.8	87.2	44.7	93.5
4.0	84.2	47.0	97.2

Table 5: REFLECTION OF TRIAL #94 COMPARED TO THINNER AND THICKER FILMS

Table 6

Specular reflection in terms of a plane, polished aluminum mirror.

Wavelength in microns	Trial #94	#94 with oxides doubled	#94 with oxides tripled
0.4	57.0	33.3	27.8
0.5	31.0	19.6	19.6
0.6	33.7	37.7	44.3
0.8	52.2	32.8	34.4
1.0	61.2	23.6	38.2
1.2	72.7	21.2	32.4
1.4	82.0	31.0	28.5
1.6	96.0	40.0	21.4
1.8	96.7	46.0	35.1
2.0	96.6	50.7	42.5
2.2	95.5	50.7	45.4
2.4	95.0	53.2	46.8
2.6	97.8	53.7	46.4
2.8	94.5	50.8	42.7
3.0	81.7	50.7	42.2
3.2	81.0	50.0	40.3
3.4	91.8	47.4	40.8
3.6	91.6	49.3	40.3
3.8	87.2	46.8	38.4
4.0	84.2	47.1	53.0

Table 6:   REFLECTION OF TRIAL #94 COMPARED TO FILMS CONTAINING

INCREASED OXIDES

22

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Table 7

Specular reflection in terms of a plane, polished aluminum mirror.

	Trial Number 94 with double:			
Wavelength in microns	Bi	Cr	Si	Ba
0.4	55.6	61.0	50.0	33.3
0.5	37.3	41.2	31.4	23.6
0.6	54.1	55.8	39.4	36.1
0.8	57.4	57.4	42.7	32.8
1.0	63.3	67.2	51.5	38.2
1.2	69.0	71.8	56.3	43.7
1.4	73.3	80.3	63.5	49.4
1.6	77.2	87.0	70.0	52.8
1.8	79.8	90.5	74.4	55.4
2.0	83.6	93.1	79.5	57.6
2.2	87.0	94.8	83.1	58.5
2.4	93.7	96.2	86.0	59.5
2.6	94.2	98.6	88.5	60.8
2.8	95.0	100.0	91.8	60.7
3.0	95.7	101.0	93.0	62.0
3.2	96.0	100.0	94.5	62.5
3.4	98.7	101.0	96.0	61.8
3.6	98.5	101.0	100.0	64.2
3.8	98.0	100.0	98.0	64.0
4.0	100.0	103.0	100.0	64.8

Table 7:   REFLECTION OF TRIAL #94 WITH DOUBLED BISMUTH, CHROMIUM,

SILICON AND BARIUM

23

Table 8

Specular reflection in terms of a plane,'polished aluminum mirror.

Wavelength in microns	Trial #94	#94 with double Bi	#94 with double Bi 10% Pd	#94 with double Bi 20% Pd
0.4	57.0	55.6	63	31
0.5	31.0	37.3	49	27
0.6	33.7	54.1	44	23
0.8	52.2	57.4	45	23
1.0	61.2	63.3	47	26
1.2	72.7	69.0	54	28
1.4	82.0	73.3	60	33
1.6	96.0	77.2	69	39
1.8	96.7	79.8	72	41
2.0	96.6	83.6	75	46
2.2	95.5	87.0	79	52
2.4	95.0	93.7	78	54
2.6	97.8	94.2	81	56
2.8	94.5	95.0	74	56
3.0	81.7	95.7	79	61
3.2	81.0	96.0	82	62
3.4	91.8	98.7	81	65
3.6	91.6	98.5	78	67
3.8	87.2	98.0	81	72
4.0	84.2	100.0	74	68

Table 8:   REFLECTION OF TRIAL #94 WITH DOUBLED BISMUTH; WITH DOUBLED

BISMUTH AND WITH PALLADIUM SUBSTITUTED FOR GOLD

24

Table 9

Specular reflection in terms of a plane, polished aluminum mirror.

Wavelength in microns	Trial #94	Cr X 2	Trial #94 with Cr X 4	Cr X 6	Cr X 8
0.4	57.0	61.0	55.0	65.0	65.0
0.5	31.0	41.2	41.8	43.7	49.2
0.6	33.7	55.8	63.8	47.8	52.3
0.8	52.2	57.4	55.4	64.6	66.2
1.0	61.2	67.2	64.5	71.0	72.4
1.2	72.7	71.8	68.0	71.8	70.5
1.4	82.0	80.3	75.0	80.0	78.8
1.6	96.0	87.0	77.0	81.2	81.0
1.8	96.7	90.5	80.8	84.7	83.4
2.0	96.6	93.1	83.2	88.3	85.8
2.2	95.5	94.8	86.4	90.2	87.6
2.4	95.0	96.2	89.3	92.7	90.5
2.6	97.8	98.6	91.6	95.3	94.0
2.8	94.5	100.0	97.4	99.0	97.5
3.0	81.7	101.0	92.2	96.2	94.8
3.2	81.0	100.0	92.2	97.3	96.0
3.4	91.8	101.0	95.0	96.4	95.2
3.6	91.6	101.0	92.0	97.3	96.0
3.8	87.2	100.0	94.4	98.1	94.4
4.0	84.2	103.0	95.0	99.0	97.5

Table 9:   REFLECTION OF TRIAL #94 WITH CHROMIUM INCREMENTS

25

Table 10

Specular reflection in terms of a plane, polished aluminum mirror.

Wavelength in microns	#94 with Cr X 4 and		#94 with Cr X 6 and		#94 with Cr X 8 and	
	10% Pt	20% Pt	10% Pt	20% Pt	10% Pt	20% Pt
0.4	45.0	35.0	40.0	45.0	60.0	20.0
0.5	40.0	29.1	29.1	36.4	49.1	21.9
0.6	37.5	26.2	25.0	34.0	48.8	21.6
0.8	47.7	30.8	33.9	41.5	60.0	23.1
1.0	55.3	35.5	40.8	46.0	68.5	25.0
1.2	57.7	37.2	45.2	48.8	69.3	26.9
1.4	66.3	43.8	50.0	53.8	76.2	33.8
1.6	70.3	46.0	52.7	56.7	78.4	36.5
1.8	74.3	50.0	57.7	60.3	82.0	39.8
2.0	78.0	54.6	59.8	63.7	83.0	40.3
2.2	80.3	56.8	61.7	65.5	85.2	42.0
2.4	84.5	59.6	64.3	70.3	87.0	42.8
2.6	88.0	64.3	69.0	72.7	94.0	44.1
2.8	92.5	68.4	74.7	76.0	95.0	44.3
3.0	88.2	65.8	71.0	75.0	92.1	43.4
3.2	88.3	66.3	70.2	72.8	91.0	40.3
3.4	87.8	69.5	73.2	75.6	94.0	40.3
3.6	88.0	68.0	74.7	73.3	90.7	38.7
3.8	86.8	68.0	77.4	73.6	92.5	39.6
4.0	85.0	67.5	75.0	72.5	92.6	35.0

Table 10:   REFLECTION OF TRIAL #94 WITH CHROMIUM INCREMENTS AND

PLATINUM SUBSTITUTION FOR GOLD

Table 11

Specular reflection in terms of a plane, polished aluminum mirror. These films were applied by brushing.

Wavelength in microns	#94	#165-A	#165-B	#165-C	#165-D
0.3	50	50	50	50	70
0.4	50	59	56	56	63
0.5	45	53	50	45	55
0.6	52	52	47	48	55
0.8	64	60	60	57	64
1.0	71	69	62	62	69
1.2	76	73	66	68	75
1.4	84	81	79	79	82
1.6	90	85	83	83	84
1.8	98	89	90	89	87
2.0	100	90	93	92	90
2.2	100	89	89	92	92
2.5	92	97	96	96	98
3.0	95	98	97	99	99
4.0	98	99	97	98	98
5.0	99	98	97	97	97
6.0	100	99	98	98	98
8.0	102	98	97	97	97
10.0	102	98	98	97	98
12.0	103	99	98	97	97
14.0	103	99	99	99	98
15.0	103	100	101	101	102

Table 11: REFLECTION OF TRIALS #94 AND #165 FROM 0.3 TO 15.0 MICRONS

Table 12

Transmission of the film plus glass in air. These films were applied by brushing. Table 2 lists transmission values for the blank glass.

Wavelength in microns	#94	#165-A	#165-B	#165-C	#165-D
0.4	0.2	0.6	0	0	0
0.5	0.6	1.7	0.4	0.4	0.2
0.6	0.1	0.4	0.1	0.1	0.1
0.7	0	0.1	0	0	0
0.8	0.1	0.1	0	0	0
0.9	0.1	0.2	0	0	0.1
1.0	0	0.2	0	0	0
1.1	0.1	0.4	0.2	0.2	0.2
1.2	0.1	0.4	0.1	0.1	0.1
1.3	0.2	0.4	0.1	0.1	0.1
1.4	0.2	0.4	0.1	0.1	0.1
1.5	0.1	0.3	0	0	0.1
1.6	0.1	0.4	0	0	0
1.8	0.1	0.5	0.1	0.1	0
2.0	0.2	0.6	0.1	0.1	0

Table 12: TRANSMISSION OF TRIALS #94 AND #165

28

Table 13

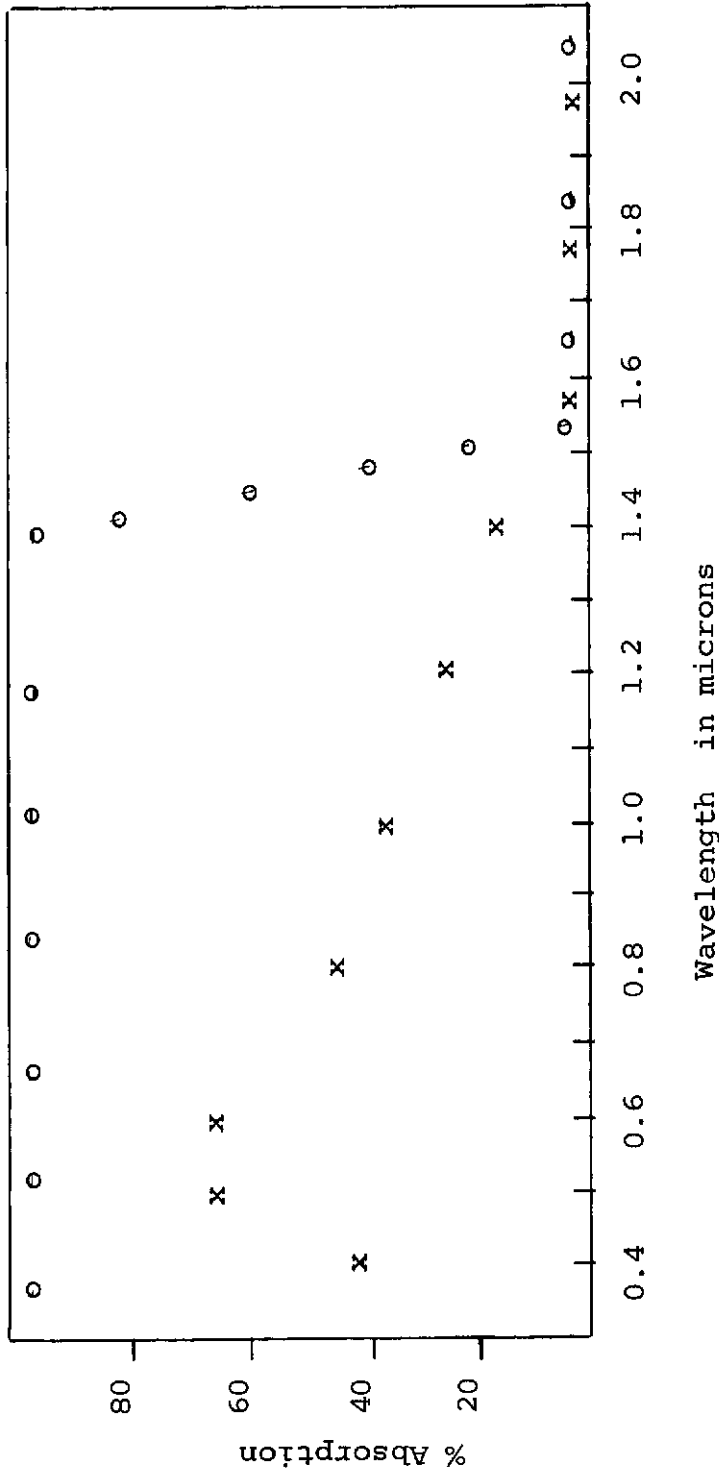|	Parts by weight
Gold sulforesinate dissolved in a mixture of oil of rosemary, nitrobenzene and toluene (24% Au)	8.99
Rhodium sulforesinate dissolved in a mixture of oil of rosemary, nitrobenzene and toluene (1% Rh)	.97
Bismuth resinate dissolved in a mixture of essential oils (5% Bi_2O_3)	2.15
Chromium resinate dissolved in a mixture of cyclohexanone and oil of turpentine (3% Cr_2O_3)	.165
Silicon resinate dissolved in a mixture of essential oils (20% SiO_2)	.209
Barium resinate dissolved in a mixture of essential oils (13% BaO)	.692
Asphalt dissolved in oil of turpentine (30% asphalt)	2.95
Rosin dissolved in oil of turpentine (50% rosin)	2.95
Hexalin	3.924
Toluene	1.0
Ethyl Acetate	1.0
	25.000

Table 13: ORGANIC CONSTITUENTS OF TRIAL #94

29

Table 14

|	Parts by weight
Gold sulforesinate dissolved in a mixture of oil of rosemary, nitrobenzene and toluene (24% Au)	13.49
Rhodium sulforesinate dissolved in a mixture of oil of rosemary, nitrobenzene and toluene (1% Rh)	1.45
Bismuth resinate dissolved in a mixture of essential oils (5% Bi_2O_3)	3.23
Chromium resinate dissolved in a mixture of cyclohexanone and oil of turpentine (3% Cr_2O_3)	.25
Silicon resinate dissolved in a mixture of essential oils (20% SiO_2)	.31
Barium resinate dissolved in a mixture of essential oils (13% BaO)	1.04
Asphalt dissolved in oil of turpentine (30% asphalt)	1.3
Rosin dissolved in oil of turpentine (50% rosin)	1.3
Hexalin	1.77
Toluene	.43
Ethyl Acetate	.43
	25.00

Table 14:   ORGANIC CONSTITUENTS OF TRIAL #165

Figure 1: CALCULATED ABSORPTION OF TRIAL #94

o = ideal solar absorption
x = calculated absorption of trial #94

N.B.   Percent absorption is an approximation calculated from the values given
in Table 4 by subtracting percent specular reflection plus transmission
from unity.

31
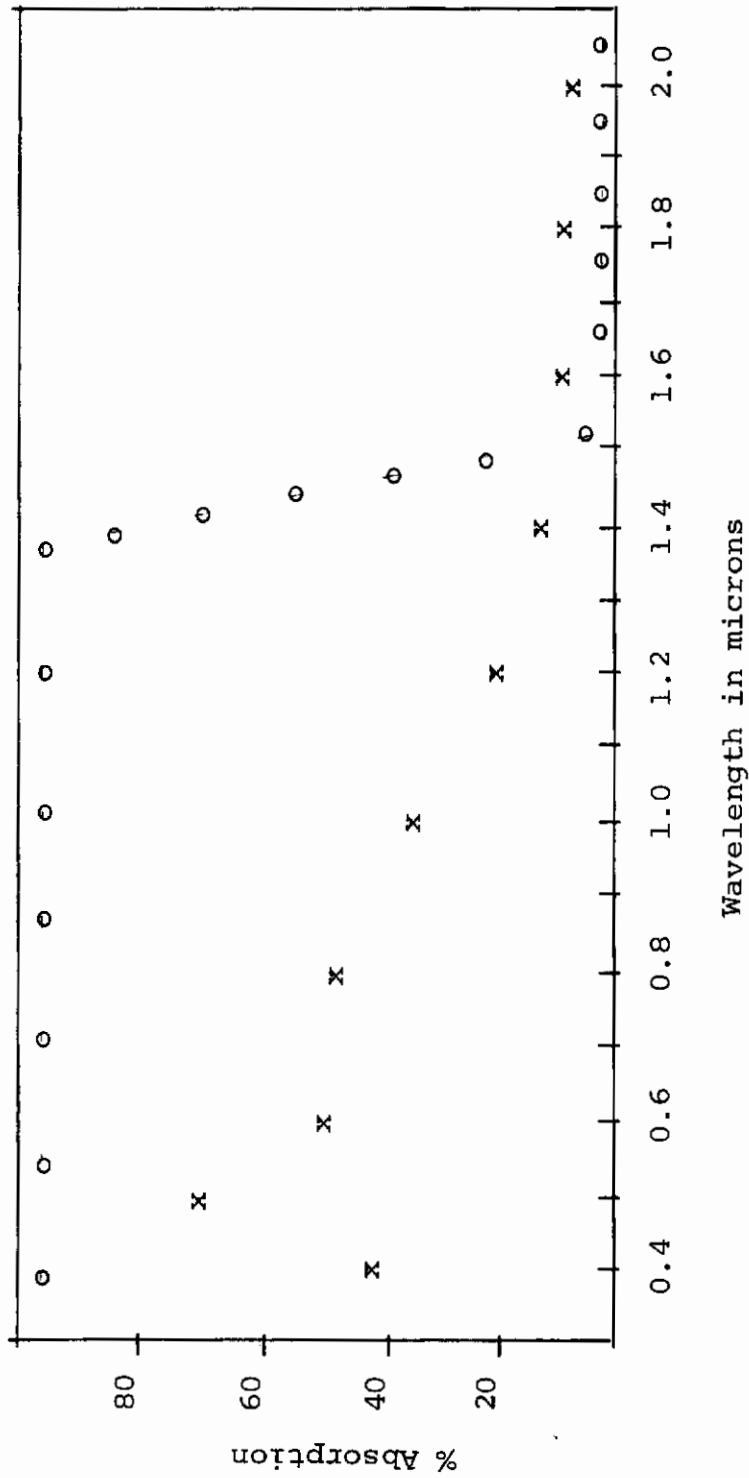
Figure 2: CALCULATED ABSORPTION OF TRIAL #165

o = ideal solar absorption
x = calculated absorption of trial #165

N.B.   Percent absorption is an approximation calculated from the values given
in Table 5 and Table 12 by subtracting percent specular reflection plus
transmission from unity.

32

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