45P

UNCLASSIFIED

N64-27387

Code-1 Cat. 19

TMX 56412

Lexington Laboratories, Inc.

35 CAMBRIDGE PARKWAY
CAMBRIDGE 42, MASS.
KIRKLAND 7-1040

FEASIBILITY STUDY OF VARIOUS ABSORBTIVITY OXIDES AS AN AID TO SATELLITE TEMPERATURE CONTROL

[redacted]

Final Annual Report

Prepared by:

A. Waugh

Submitted to:

National Aeronautics and Space Administration
Goddard Space Flight Center
Greenbelt, Maryland

Contract NAS 5-582

Lexington Laboratories, Inc.
35 Cambridge Parkway
Cambridge 42, Massachusetts

24 November 1962

OTS PRICE

XEROX $ 4.60 ph

MICROFILM $

1. TABLE OF CONTENTS

1.	TABLE OF CONTENTS	i
2.	FIGURES AND TABLES	ii
3.	BRIEF SUMMARY	iii
I.	INTRODUCTION	1
II.	GENERAL PHOTOTROPIC BEHAVIOR IN RELATION TO FEASIBLE SATELLITE TEMPERATURE CONTROL SYSTEMS	5
III.	SURVEY WORK	8
	a. Crystalline Materials	9
	b. Glasses	13
IV.	FEASIBILITY STUDIES	18
	a. Coating Techniques	18
	b. Reproducibility in Barium Titanate Ceramics	19
	c. Thermal Reversibility in Barium Titanate Ceramics	20
V.	PHOTOTROPY IN BARIUM TITANATE	24
	a. Firing Atmosphere Effects on Reproducibility	24
	b. Kinetics of Darkening	27
	c. Phototropy in other lots of Commercial Barium Titanate	32
	d. Pure Barium Titanate	33
	e. Spectral Dependence of Darkening	34
	f. Spectral Dependence of Bleaching	35
VI.	MECHANISM OF PHOTOTROPY	36
VII.	CONCLUSION	39
	REFERENCES	40

2. FIGURES AND TABLES

Table I - Phototropic Response of Some Surveyed Materials 11

Figure 1 - Fabrication of Phototropic Coating $BaTiO_3$ + Sodium Silicate on Aluminum 10

Figure 2 - Darkening under standard source irradiation for $BaTiO_3$. Commercial grade lot 7C. TAM 21

Figure 3 - Bleaching curves without irradiation $BaTiO_3$ commercial lot 7C. TAM 22

Figure 4 - Darkening and Bleaching of $BaTiO_3$ commercial grade Lot 7C TAM 23

Figure 5 - Darkening curves for $BaTiO_3$ fired in vacuum at 1200°C for 1 1/2 hrs. 25

Figure 6 - $BaTiO_3$ Commercial grade lot 7C TAM, Firing treatment effects on darkening curves 26

Figure 7 - Darkening curve for C.P. $BaTiO_3$ Lot 30C TAM 31

27387

3. BRIEF SUMMARY

Our research during the past year has been divided into four general categories. They are: (1) A survey of materials to determine which ones exhibit phototropy, (2) Evaluation of the feasibility of their use as coatings for satellite temperature controls, (3) Optimization of their behavior for potential use, and (4) Study of the mechanism by which phototropy occurs.

Our survey of materials has undergone an alteration in objective for two reasons. First, the necessary stability in high vacuum in outer space has led us to concentrate attention on materials which exhibit phototropy in bulk rather than as superficial reactions. Secondly, the recognition that higher bleach temperatures than 70°C (the limit imposed by the assumption that the required bleach temperature must be equivalent to the operating temperature for transistors and other electronic apparatus) has led us to examine more stable compounds and their behavior at high temperatures.

Feasibility of using existing phototropes for partial satellite temperature control has been demonstrated for barium titanate-base materials. We have shown that coatings of barium titanate powder can be applied to aluminum panels with the use of sodium silicate cement without reducing the phototropic response of the coating. We have also recognized that even though changes in reflectance observed for many phototropes are small, when coupled with high initial reflectance, the change in

Author

the α/e ratio may provide a substantial degree of control through wide exursions in the solar constant.

Optimization of properties in existing phototropes by adjustment of chemical composition has been indicated from our quantitative measurements of darkening and bleaching kinetics and the temperatures at which no darkening occurs under irradiation. Two different procedures for examining the phototropy with respect to composition in a given phototrope have been recognized as reasonable approaches to the optimization of properties. Both were begun toward the end of this contract year and will be pursued further in the coming year.

The survey of materials, feasibility of their use, and judgement of direction of optimization have been based on quantitative measurements of: reflectance changes under irradiation, thermal reversibility in the dark and under irradiation, and the kinetics of darkening and bleach reactions. These measurements have been supplemented by: conductivity measurements, oxidation and reduction effects, the dependence of darkening and bleaching rates on the wavelength of irradiation, and the reflectance spectra at low temperatures as well as room temperature to provide information on the mechanism of phototropy. These data have shown that the absorbing centers produced in titanate-base phototropes are either highly localized (that the jump distance between trapping sites are very short range) or that the migrating species is chargeless. We hope to determine whether excitons, polarons, or chargeless interstitial ions are the responsible species in further studies.

I. INTRODUCTION

During the past year the criteria upon which material selection for practical satellite temperature control were based have been re-examined. It had previously been assumed that the upper temperature limit at which the controlling phototropic material could operate was in the range of 70°C. This temperature was selected from the maximum temperature at which transistors and other electronic apparatus would operate reliably. Because the temperature of the satellite is an average of the surface temperatures of the bright side and the dark side, it is clear that the temperature of the bright side can be somewhat above 70°C while maintaining the interior temperature at 70°C. By utilizing appropriate areas on the satellite on which the phototropic material and non-phototropic materials are distributed, it is possible to operate the satellite at a desired temperature while the controlling phototropic material could operate at a significantly higher temperature. The appropriate satellite temperature is achieved by simply selecting the relative area required in order to permit the controlling phototropic material to operate at its required temperature, with the bleaching rate in equilibrium with the darkening rate. One of the limitations encountered so far in screening materials for potential use was that the bleach temperatures or reversal temperatures were apparently higher than 70°C. In fact, for most of the materials examined, they either did not bleach within the temperature range investigated or increased in

darkening rate with increasing temperature within the range of temperatures investigated. For the phototropic material to control temperature, it must undergo thermal bleaching and must be operated at a temperature range where the bleaching rate and darkening rate are nearly in equilibrium. With recognition that the phototropic material could operate at a higher temperature and still provide temperature control for the satellite, the literature was re-examined to determine known thermal bleaching characteristics for phototropic materials. It was learned that a significantly larger body of literature exists on phototropic materials and their bleaching behavior than was appreciated at the beginning of the year.

With the restatement of the criteria upon which material selection can be made, the experimental program was modified in order to investigate the higher temperature characteristics of phototropes. The higher temperature experimental work which has been undertaken has provided us with several important results with respect to the objectives of this program:

1. By utilizing a coating consisting of two materials to control the temperature to a bleach temperature in an existing phototrope, some temperature control is now possible.

2. By extending the survey to higher temperatures, most materials have been found to undergo thermal bleaching; some materials undergo further darkening. The latter are unsuitable for cyclic temperature control.

3. The complexity of bleaching in $BaTiO_3$ (observed at the higher temperatures) has indicated the possibility of optimizing the bleaching behavior for temperature control.

During this year we have appreciated the important distinction between phototropy as a superficial phenomenon and as a bulk phenomenon. For the materials which exhibit phototropy at the surfaces, it has been reported in the literature that these are frequently strongly dependent upon the environment. As a consequence of the anticipated different behavior in the hard vacuum in space in comparison with laboratory experimental work, phototropic materials with only superficial reaction have been given low priority with respect to the objective of this program. As a corollary, materials which exhibit phototropy in bulk, which are stable with respect to a space environment up to several hundred degrees Centigrade would appear to be suitable for long-time satellite temperature control. Consequently, the program for the elucidation of phototropy mechanisms has been focussed on materials which exhibit phototropy in bulk.

The phototropic behavior of glasses has been attributed in a number of cases to the presence of pairs of impurities rather than single impurities. The alteration under irradiation results presumably from electron transfer between pairs of impurity or additive ions. The electron transfer then alters the spectral transmission of both. The need for pairs of appropriate additives suggests that the crystalline hosts for such defects, which in the work performed thus far have been doped with single additives, might also exhibit enhanced phototropy if pairs of additives were introduced. In general, for the

glasses and crystalline materials which have exhibited phototropy, there are pairs of ions present which can undergo change in valence. Thus, in the titanates the interaction may result between single impurities or additives and the titanium ions in the matrix. Phototropy may also result in pure stoichiometric materials because of the presence of anion vacancies at which electrons can be trapped. Because of the multiplicity of kinds of defects between which electron transfer can cause optical changes, it is now appreciated that the need for this program is for a specific statement of the kinds of matrices and defects from which maximum phototropic response can be achieved. The program on the investigation of the mechanism of phototropy and on the survey of dopants and hosts was realigned to this objective.

II. GENERAL PHOTOTROPIC BEHAVIOR IN RELATION TO FEASIBLE SATELLITE TEMPERATURE CONTROL SYSTEMS

In the previous year, phototropy was considered as an isolated phenomenon. The distinction between phosphors, thermoluminescent materials and phototropes is not clear-cut. Consequently, the physical interpretation of phototropy can be greatly strengthened by the realization that considerably greater effort has been expended on phosphors and that the differences between the concentration and stability of trapping levels and the specificity of emissive decay are only minor alterations on the broad basis of band theory and defect states on which all of these phenomena may be qualitatively understood.

There are several different ways in which the optical transmission can change under irradiation (1). One typical change is a shift in an absorption peak that exists in the middle of a transmission region. Another change is to introduce an absorption peak in the middle of the spectrum of interest where none existed previously. The third typical change in transmission might be a change in the dispersion at the absorption edge. Another change observed in some glasses is to decrease the u.v. absorption while increasing the absorption in wavelengths beyond the u.v. cut-off. Finally, some materials exhibit absorption of fairly uniform magnitude over a wide range of wavelengths. These are the kinds of absorption property changes observed in typical phototropic materials. Use as a suitable satellite

temperature control material is dependent upon a sufficiently large thermally reversible change in absorption coefficient.

In addition to the thermal bleaching which has been reported for a number of materials that exhibit phototropic behavior, it has also been observed that in general a longer wavelength irradiation than the wavelength required for the darkening reaction will bleach the material (1). For instance magnesium oxide with iron impurity has been reported to undergo a coloration on exposure to X-rays which bleaches out entirely if the sample is exposed to normal room illumination at room temperature (2). Hackmenite, has also been reported to undergo a strong red coloration upon exposure to an iron spark which bleaches completely with 30 seconds exposure to a tungsten lamp at room temperature (3). Uranium and iron-bearing glazes which also contain titanium have been reported to undergo bleaching or a reduction in coloration upon exposure to normal illumination (4). Coloration is restored upon storage in the dark for a period of a day in room temperature. Similar color bleaching was observed in one of the glasses prepared and described below during illumination to a normal solar spectrum. For this reason, it would appear that the illumination under normal sunlight is a more restrictive criterion for the occurrence of phototropy than is necessary for the fabrication of workable control systems. For instance, if a material in which phototropy is inhibited by the simultaneous irradiation by all of the longer wavelengths which occur in the solar spectrum were used beneath band pass filter, the darkening reaction could be significantly enhanced

because of the exclusion of the longer wavelengths which would ordinarily cause bleaching. The use of such a band pass filter would reduce the total amount of energy upon which the control system is working and would consequently reduce the total temperature control possible. Recognizing that phototropic materials exist which would normally bleach with longer wavelength irradiation means that the spectral dependence of darkening and bleaching must be measured to characterize phototropes.

III. SURVEY WORK

Our survey work during this year included measurements on glasses, on solid solutions of sodium chloride and silver chloride, on mercury salts, various lots of barium, strontium, and calcium titanates obtained from TAM, and organic compounds with potential use as a cement for inorganic materials, and finally of the effect of coating techniques on phototropy in barium titanate lots which had exhibited the highest phototropy observed to date.

The sodium chloride-silver chloride solid solutions were prepared in the composition range from 0-15 mol % silver chloride. Stokes observed that sodium chloride silver chloride homogeneous solid solutions formed at high temperatures exhibited ex-solution at low temperatures with the peak temperature of the two-phase region at approximately 180°C. He also noted that at room temperature samples exposed to light exhibited photosensitivity. The work performed here was based on an assessment of the usual shape of the two-phase region to be expected from typical ex-solution behavior. Typically, the temperature at which the system changes from a single phase equilibrium structure to a two-phase equilibrium structure will decrease with change in composition away from the maximum. Consequently, since the maximum temperature was known to be 180°C at ~50 mol % silver chloride, compositions containing small amounts of silver chloride were investigated to determine at what composition the photosensitivity occurred at room

temperature. It was anticipated that for potential use, the mixture which was precipitated by a photoactivated reaction would upon increasing absorbance tend to raise the temperature back to the phase boundary at which the precipitated component would re-enter solid solution.

Mixtures of sodium chloride and silver chloride were melted at high temperatures and then slowly cooled. The samples were crushed and pressed with Lucite to form pellets for reflectance measurements. The reflectances were run as cooled and after exposure to the standard solar source. Samples containing less than 10 wt % silver chloride did not exhibit any change in reflectance upon exposure at room temperature. The samples containing 15 mol % silver chloride exhibited substantial darkening as shown in Figure 1. We have not completed measurements on equilibrium reflectance as a function of temperature or bleaching characteristics to determine the utility of this material.

a. Crystalline Materials

We have measured the initial reflectance and the darkening behavior in lead titanate ceramics, cerium titanate ceramics, iron-doped ceramics and copper-doped barium titanates in addition to some preliminary work on mixtures of strontium and barium titanates. The reflectances, the change in reflectance, and maximum change in absorbance (1-R) for these mateials are shown in Table I. For most of these materials the changes in reflectance are insufficient or the initial

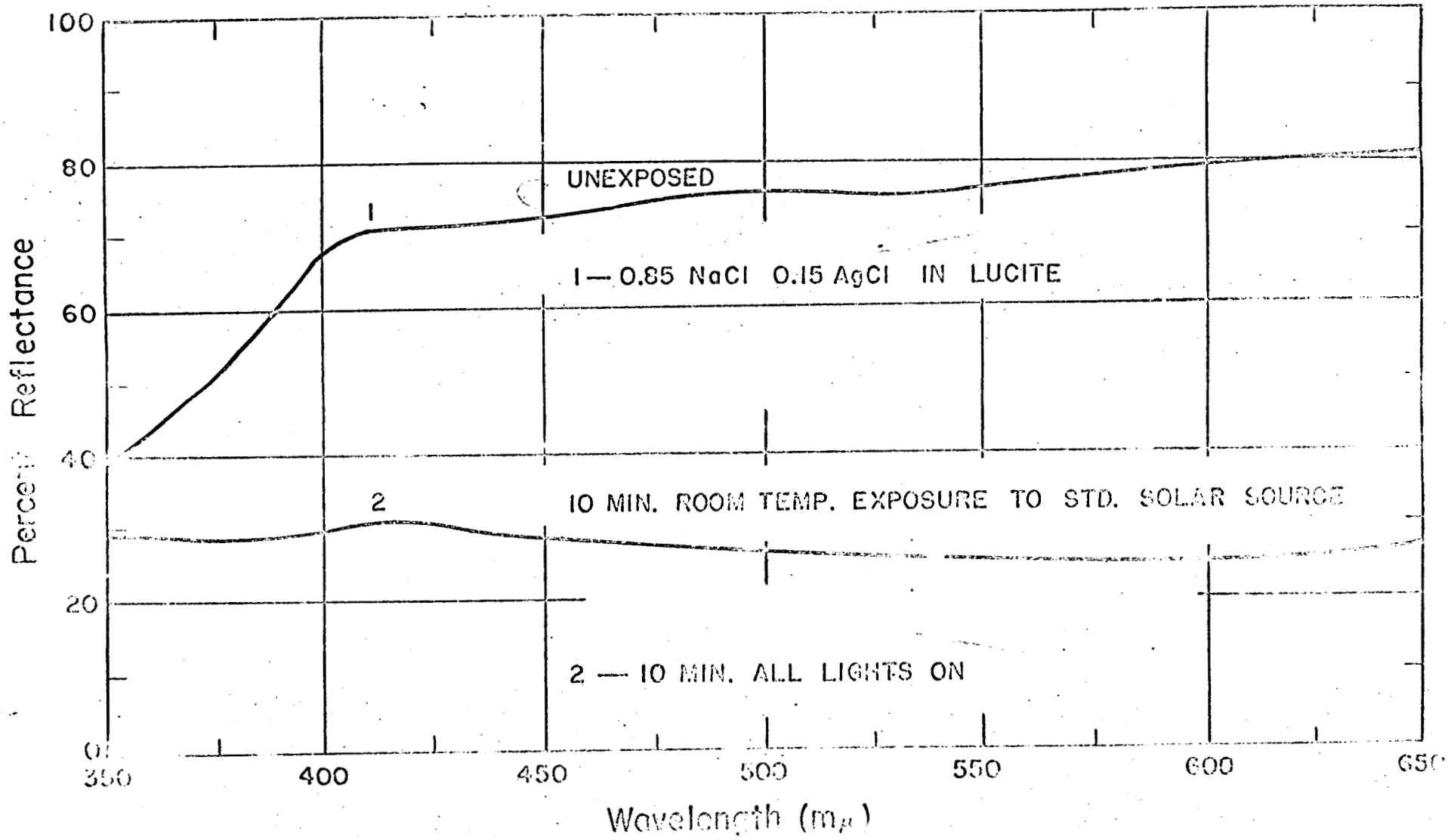

Fig. 1: Darkening behavior of a NaCl AgCl mixture.

TABLE I

Phototropic Response Of Some Surveyed Materials

	R%	ΔR%	Absorbance*
$PbTiO_3$	90	8	1.8:1
$CaTiO_3$	45	2	1.1:1
Sr-$BaTiO_3$ mixes 1)	85	20	2.3:1
2)	50	10	1.2:1
$BaTiO_3$			
Commercial Grade	80	40	3:1
	85	50	4:1
High Purity	95	12	3:1
	98	12	8:1
$CaTiO_3$ pure	88	28	3.3:1

*Ratio of absorbance in darkened state to absorbance in bleached state

reflectances are too low to show promise for potential use in satellite temperature control in comparison with the effects observed in barium titanate. Strontium titanate—barium titanate mixtures were prepared because it was observed that thermal bleaching in barium titanate coincided with the Curie temperature (115°C). Additions of strontium titanate to the barium titanate lower the transition temperature[5]. Assuming that the bleaching process is associated with enhanced electrical conduction at the transition, the bleach temperature would also be reduced by addition of strontium titanate. Partial bleaching does occur at 78°C, though total recovery was not observed until the temperature was raised to 125°C. We do not know whether these samples were completely reacted. The behavior may result from the fact that material is two-phase. In our survey work to date strontium titanate has consistently exhibited lower changes in reflectance on irradiation in both pure and doped states.

Other materials which we have examined include Titanox, (a commercial TiO_2) which was prepared with a Lucite binder. Equilibrium reflectance measurements were conducted as a function of temperature. The maximum reflectance change observed is of the order of 8% with a recovery of approximately 6% in going from 70°C to 125°C under full solar exposure. Calcium titanate specimens were prepared by firing at 1100°C and exhibited a rather large change in reflectance. A change of approximately 40% at room temperature

was further increased upon exposure at higher temperatures. That is, the calcium titanate does not exhibit bleaching at higher temperatures but enchanced darkening up to a temperature of 180°C. Another sample consisting of TAM 80-10-10 (80% $BaTiO_3$, 10% $SrTiO_3$, 10% $CaZrO_3$) exhibited a high initial reflectance, it also underwent saturation darkening within ten minutes, and partial recovery at 70°C. A sample fabricated from barium titanate lot 45-C and TAM 80-10-10 in the ratio of 2:1. Exhibited saturation darkening within 10 mins at 30°C but only 4% recovery at temperatures up to 175°C.

b. Glasses

References in the literature to darkening of glasses under normal solar irradiation are numerous (6). Extensive work was performed around 1930 on the darkening process in glasses. Most of this work had essentially opposite goals than the present program; that is, the transparency or color stability was desired to be retained during exposure to solar irradiation. The coloration in most glasses is due to the presence of arsenic or vanadium or bismuth or iron or manganese (oxides) in combination with cerium oxide. Cerium is normally introduced as a decolorizer to supress the colors introduced by impurities. Upon irradiation there is apparently an electron transfer between cerium and one of the other impurities which causes a shift in the

absorption spectrum. Unfortunately, most of the work reported on glasses is qualitative. The exposures may have ranged from periods of days to months under normal atmospheric conditions, and the appropriate selection of additives to the glass was based on suppression of coloration. As a consequence, changes in absorption coefficient are but rarely reported and further the spectral distributions of the changes occurring with irradiation are not generally available. A few glasses have been developed which undergo "intense" coloration in a short interval of time. They have been used to determine the radiation intensity at weather stations. The glasses reported by Weyl (6) for this purpose were essentially taken from the Eckert and Schmidt's report (7).

There has been little information about the speed with which the darkening reaction occurs and whether saturation occurs in a fairly short period of time.

Several glasses have been specifically developed for use as radiation monitors; these exhibit essentially linear change in absorption coefficients at a specific wavelength upon exposure to gamma-rays or X-rays. A linear relation (on a log-log plot) of absorption versus exposure has been observed up to 10^7 R.

A number of glasses were prepared during this year and the darkening and bleaching and the thermal effect on bleaching were investigated. The compositions are given in quarterly reports 6 and 7. The reflectance or transmittance for the samples prepared here was not in exact agreement with data reported in the literature. The effect of changing arsenic to ceria ratios was also not in accord with the effects reported

in the literature[6]. All glasses investigated were found to darken under ultra-violet irradiation. The maximum change in reflectance occurred at the spectral region near the UV cut-off; the change observed was approximately 45%. Over most of the spectral region investigated, 450-650 millimicrons, the change in reflectance was small. This spectral change, with maximum change in absorption coefficient near the UV cut-off is essentially identical to the effects reported by Rindone[8] who investigated the effects of changing base glass composition and the substitution of various alkali and alkaline earth oxides. Qualitatively the effects are well reproduced. The exact response or change with compositional change is not generally reproduced.

Weyl[6] has reviewed the general effects in glasses and concluded that the presence of titanium enhanced the rate and maximum solarization. On the other hand, Rindone[8] found that the presence of titanium diminished both the rate and the maximum solarization. The effect observed here was essentially intermediate and whether the titanium has a specific effect cannot be resolved. In general our results agree with other data reported in the literature that in silicate base glasses, the rate of approach to saturation and the change in reflectance or transmission over most of the visible spectrum is small. We do not know what the saturation darkening would be but it appears unreasonable to attempt to determine saturation values based on the observed changes in the time interval available for measurement. While use for temperature control for space probes does not require a very rapid approach to saturation,

experimental investigation of these low reaction materials does not appear to be warranted.

Glasses were prepared with a phosphate base activated by silver phosphate. (Reported in the literature for use as a monitor for high energy radiation.). Upon exposure for successive time intervals to the UV source, the reflectance decreases to 30-40% within 240 minutes. After darkening, the sample was heated to 300°C to determine whether or not it would thermally bleach. Instead of bleaching the reflectance decreases by an additional 15%. This suggests that the material is acting as a photosensitive glass rather than as a phototrope; the subsequent darkening with heat treatment probably results from the precipitation of silver. Crystallized segments of this same material decreased in reflectance to a value of about 35% at 500 millimicrons upon exposure to UV. Upon exposure while heating at 75, 125, and 150°C the sample exhibited further darkening rather than bleaching. Upon dark bleaching at 300°C the reflectance increased in a spectral region above 500 millimicrons as expected for a typical thermal bleaching process. For this glass the darkening process is slightly thermally activated as has been observed for a number of phototropic materials[9].

Another base glass composition consisted of a bismuth-lead-borate with 2.4% tri-oxide. This base is less interesting than other materials under investigation because its UV cut-off occurs at approximately 450 millimicrons. Consequently, the total area within the solar spectrum for which a change in absorption coefficient can occur is smaller and, therefore, the energy balance change is also smaller. Upon UV exposure, the

sample exhibited only 4% change in transmittance at 65 hours exposure. The sample was then exposed to 50 KV X-rays for artificial darkening. Upon exposure to 10,000 Roentgens the transmission decreased 15% at 550 millimicrons and 5% at 450 and 650 millimicrons. Continued darkening with exposure has been reported[10].

Our interest was to determine whether thermal bleaching would occur at a sufficiently low temperature to warrant its use for possible satellite temperature control. Samples were successively bleached at 100°C intervals up to 400°C. The recovery was erratic; increased transmittance of approximately 5% occurred up to 300°C. Upon heating to the higher temperatures transmittance decreased by 10% instead of exhibiting continued bleaching. This result is at variance with complete recovery reported in the literature[10].

These results show that some necessary chemical species required for phototropy in glasses have been identified. The lack of agreement on directions of effects and bleaching suggests that the structural aspects (which are poorly defined in glasses) may govern the behavior.

IV. FEASIBILITY STUDIES

a. Coating Techniques

In order to evaluate the feasibility of forming coatings of barium titanate, two different techniques were employed for affixing barium titanate powder coatings to aluminum panels. Aluminum panels were roughened by sand blasting and then submitted to TAM for flame spraying. Flame-sprayed coatings were formed from a lot of barium titanate which had exhibited high phototropic response. All of the coatings exhibited a darker gray color than had been observed in any of the fired ceramics prepared from the same lot. They also exhibited much lower equilibrium reflectance in the as-formed states and very much smaller changes in reflectance upon exposure to standard solar source. After one hour exposure the reflectance decreased from approximately 64% to approximately 61% in the spectral region from 400-650 millimicrons.

It is not known why the heat treatment given in flame spraying so drastically changes the phototropy exhibited by barium titanate. However, it appears at present that this is not a feasible technique for applying barium titanate coatings to aluminum. Other coatings were applied to roughened aluminum plates by coating the aluminum with waterglass, (sodium silicate) and then sprinkling the barium titanate powder onto the wet sodium silicate layer. These panels were then dried and the reflectance was measured as formed and after exposure for various

intervals to standard solar source. The reflectance changes are equivalent to those observed in ceramic specimens. We conclude that a sodium silicate binder is appropriate for achieving sufficient adherence to form a satisfactory coating and that the sodium silicate substrate does not deleteriously affect the phototropic response.

b. Reproducibility in Barium Titanate Ceramics

One of the problems with either the use of materials for satellite temperature control or for the research into the mechanism of property behavior is associated with the general reproducibility of given sets of measurements. Upon deciding that the commercial grade barium titanate appears to be the most promising material surveyed, we obtained various lots of commercial material to determine the reproducibility. We have also obtained high purity barium titanate in powdered form and fabricated specimens from these and also have secured some high density hot-pressed barium specimens for property measurements. The initial reflectance, the kinetics of darkening and the saturation darkening were equivalent to within a few percent reflectance. With the chemical analyses of these respective specimens we hoped to be able to determine which of the various impurities present are responsible for the phototropic behavior of the commercial grade material. Doping a high purity material may give even higher changes in reflectance than we now obtain in commercial grade material. Reflectance and reflectance changes can be held to within a few percent from sample to sample and lot

to lot for the lots we have examined. Whether new lots will contain different impurities at different concentrations which will change phototropic behavior is not known, but certainly is to be expected.

c. Thermal Reversibility [illegible] Barium Titanate [illegible]

A number of different runs where conducted on commercial grade barium titanate samples to determine the reversibility of phototropy. The bleaching experiments were conducted both in the dark and under full solar irradiation. Under dark bleaching the full initial reflectance can be recovered by heating to 125°C within 1 1/2 hours. Specimens cycled many times have revealed no decay in phototropic response or recovery. The specimens which were bleached under irradiation require a slightly higher temperature in order to recover the full initial reflectance, a typical curve for darkening is shown in Figure 2. Typical curves for recovery with dark bleaching is shown in Figure 3 and several curves at different temperatures for full solar irradiation are shown in Figure 4.

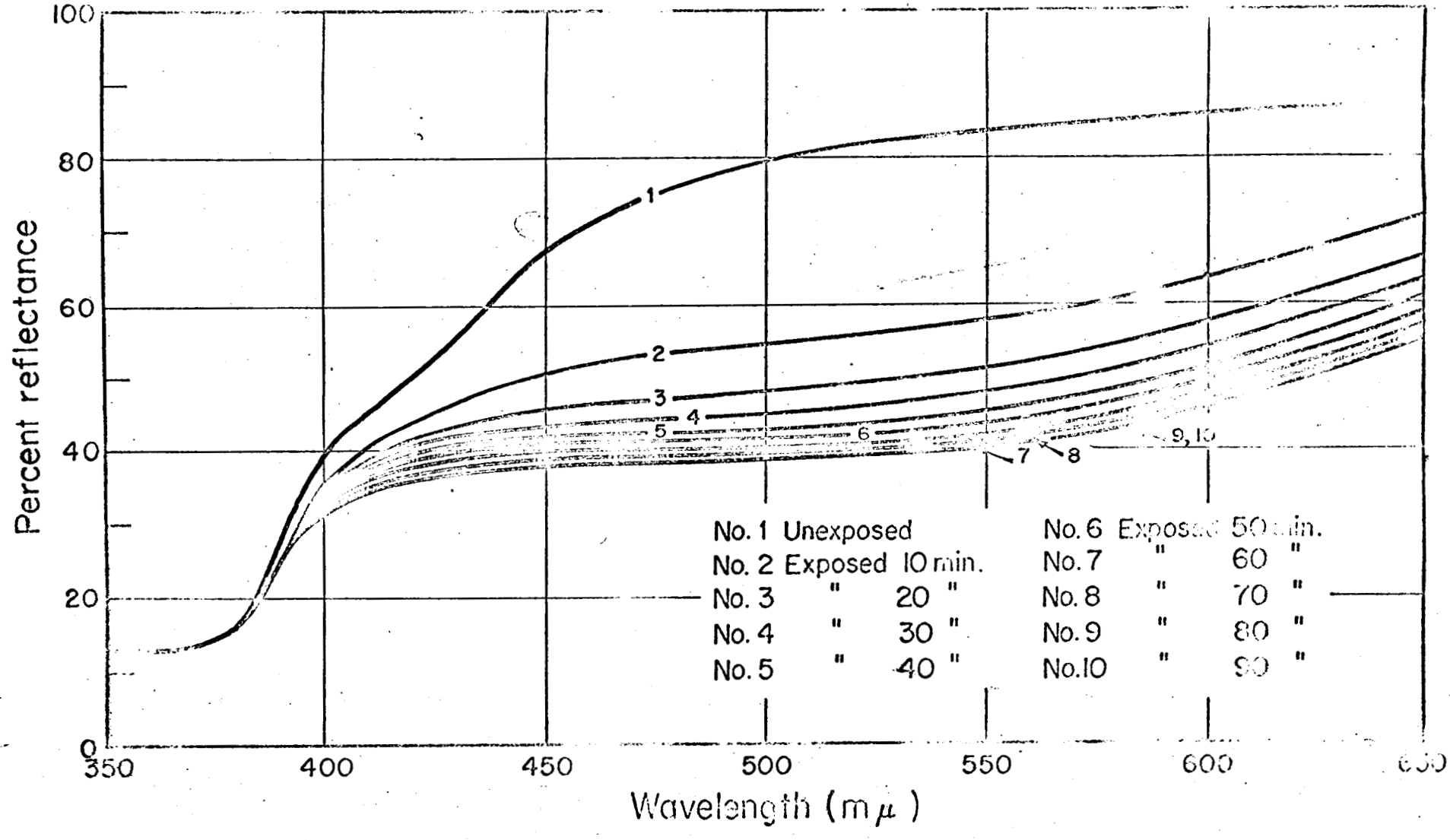

Fig. 2: Darkening under standard source irradiation for $BaTiO_3$. Commercial grade lot 76. TM

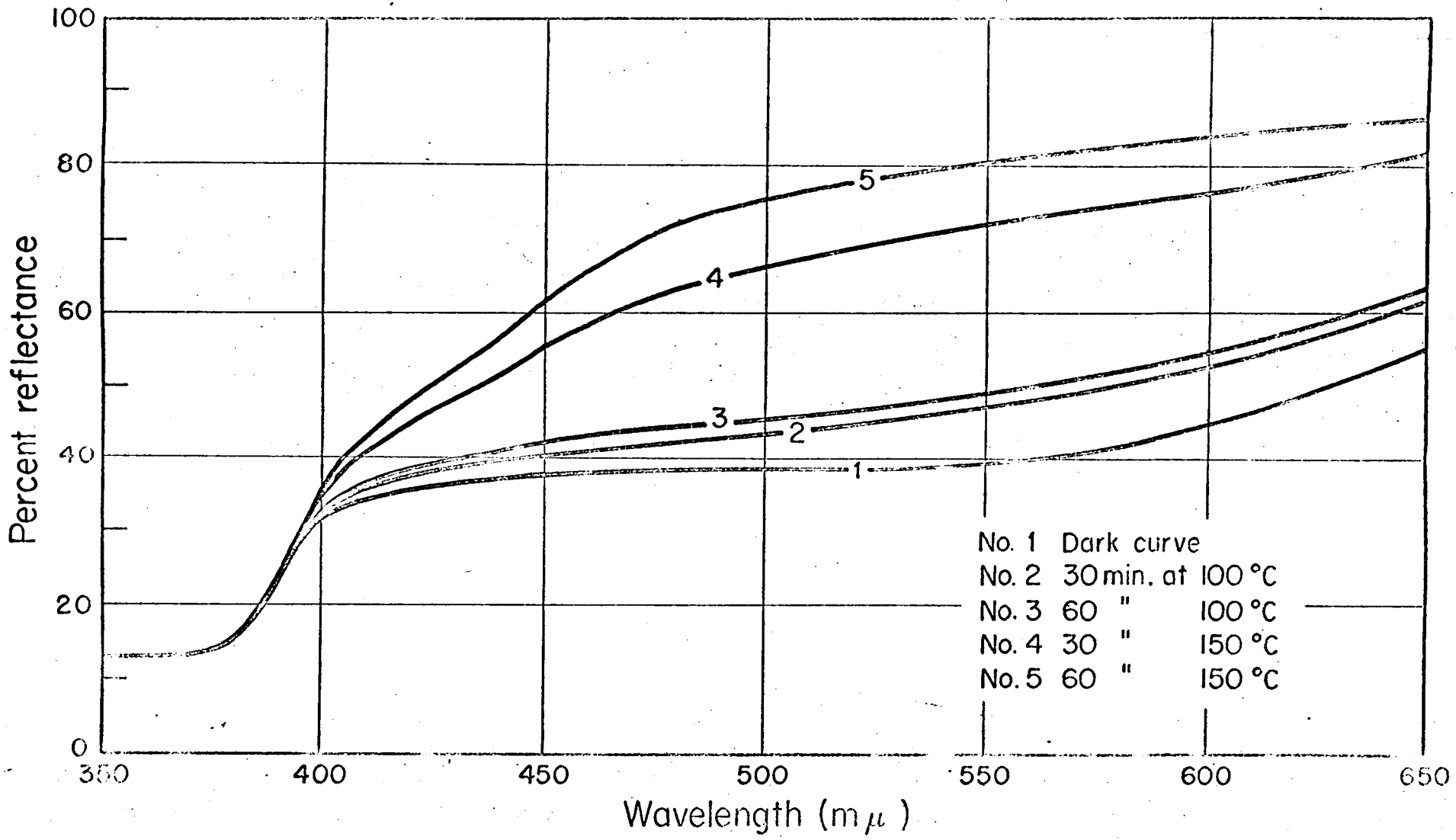

Fig. 3: Bleaching curves without irradiation
$BaTiO_3$ commercial lot 7 [illegible]

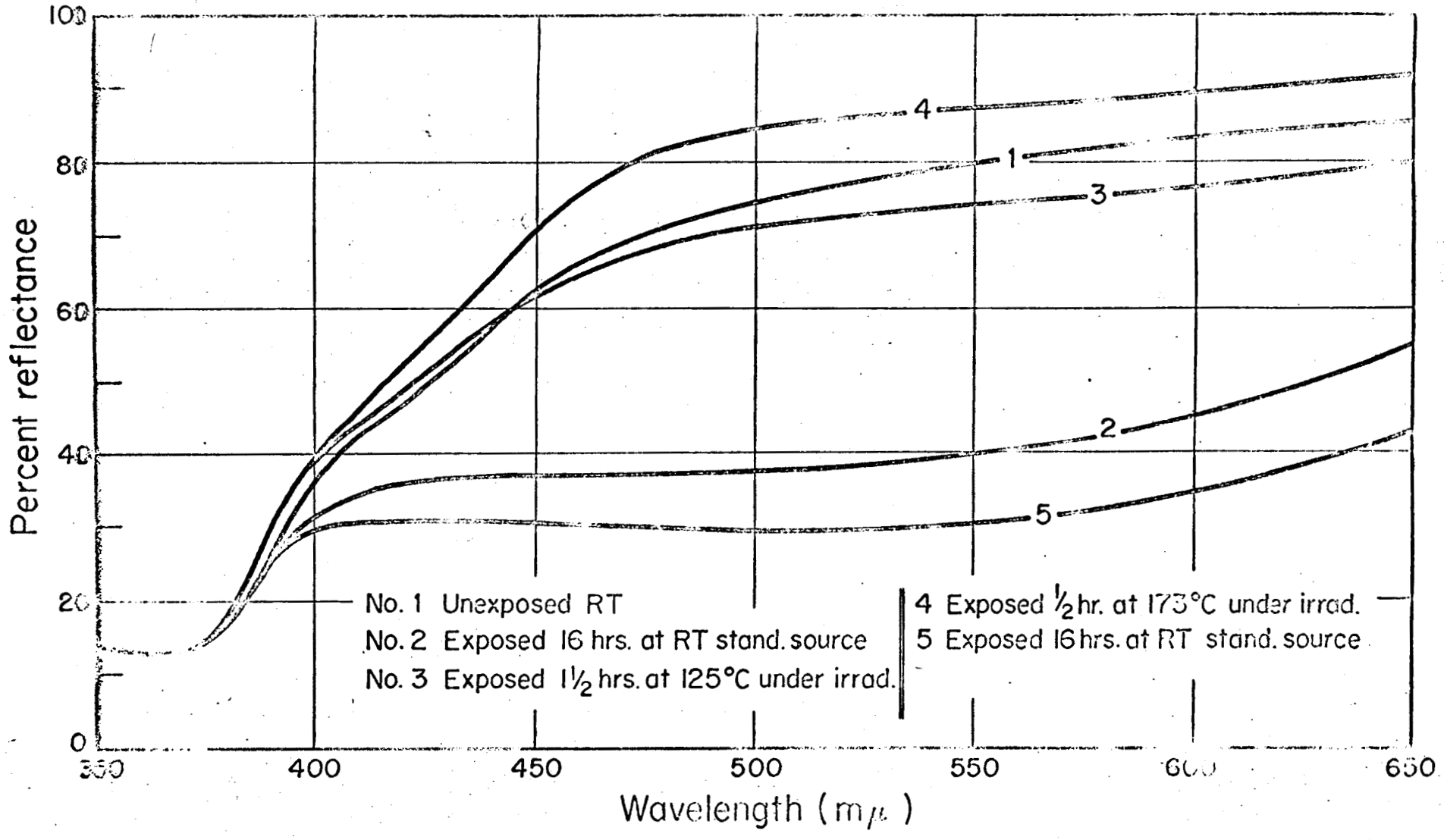

Fig. 4: Darkening and leaching of $BaTiO_3$ commercial grade Lot 79 [illegible]

V. PHOTOTROPY IN BARIUM TITANATE

a. Firing Atmosphere Effects On Reproducibility

A sample which had been fired in an oxidizing atmosphere was reduced by re-heating at 1200°C in a vacuum furnace. The reflectances in the oxidized and reduced states are shown in Figure 5. A small change in initial reflectance is observed at 390-450 millimicrons. Within this wavelength region the initial reflectance is depressed by 15% upon firing in vacuum. The spectral reflectance beyond 450 millimicrons is essentially unchanged. The phototropic darkening under full solar irradiation for the reduced state is also shown in Figure 5. It is essentially equivalent to that observed in the oxidized specimens in Figure 2. Neither the rate of change nor total darkening was effected by the reducing treatment. From this we may conclude that the reproducibility in firing barium titanate ceramics is not strongly sensitive to furnace atmosphere control. Sintering was also attempted in 10 atmospheres of oxygen. This was unsuccessful because of failure of the furnace heating winding. We had hoped to increase the reflectance in the region of 390-450 millimicrons by oxygen firing.

The sensitivity to firing treatment was also examined with respect to firing temperature and time. Standard firings have been conducted at 1200°C for approximately one and one-half hours or for prolonged periods of time (72 hours at 1262°C). (Figure 6) The initial reflectance of the as-fired specimens of commercial barium titanate decreased to approximately 30% in comparison to 80% for the normal firing cycle. Furthermore,

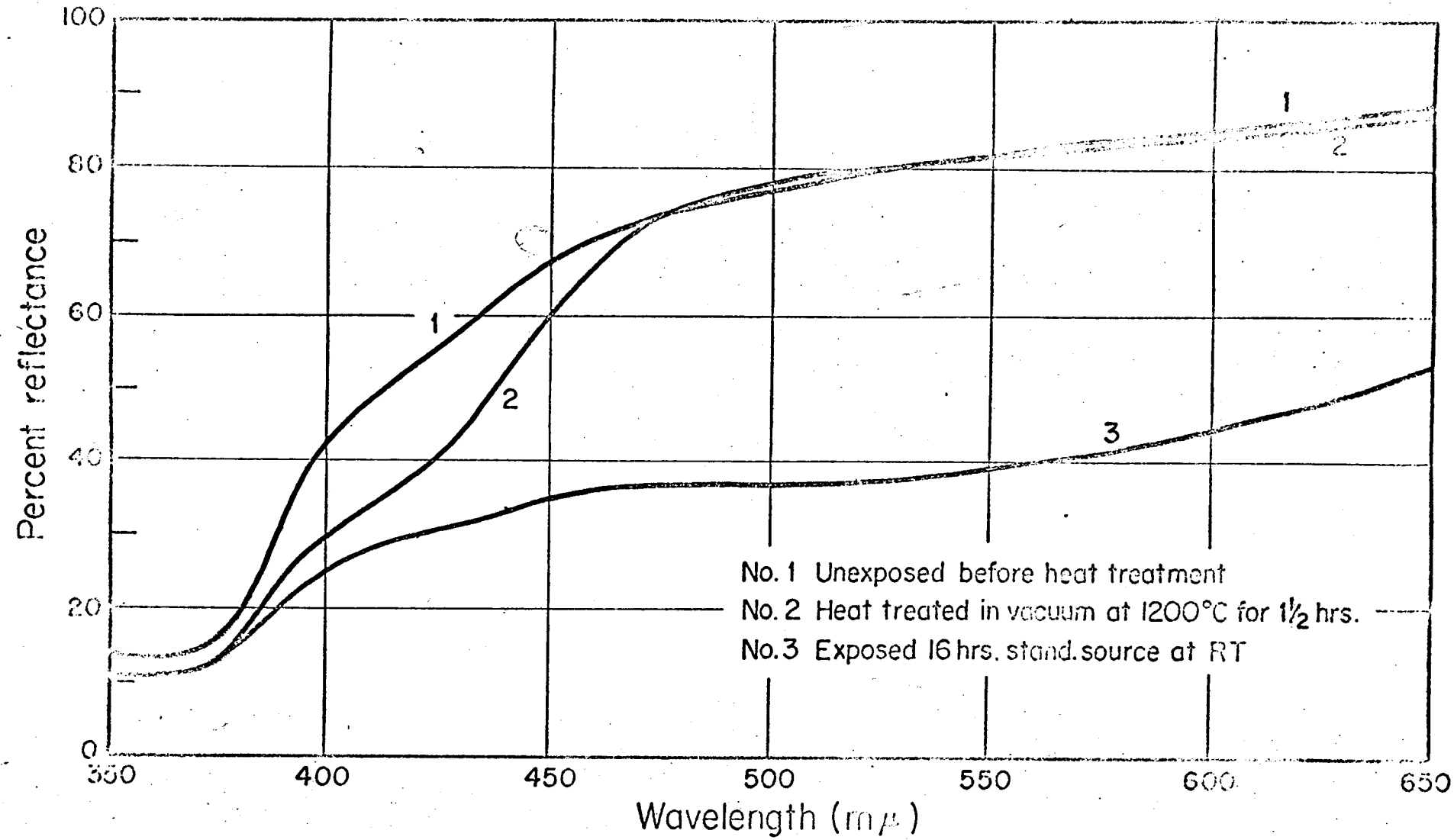

Fig. 5: Darkening curves for $BaTiO_3$ fired in vacuum at 1200°C for 1-1/2 hrs.

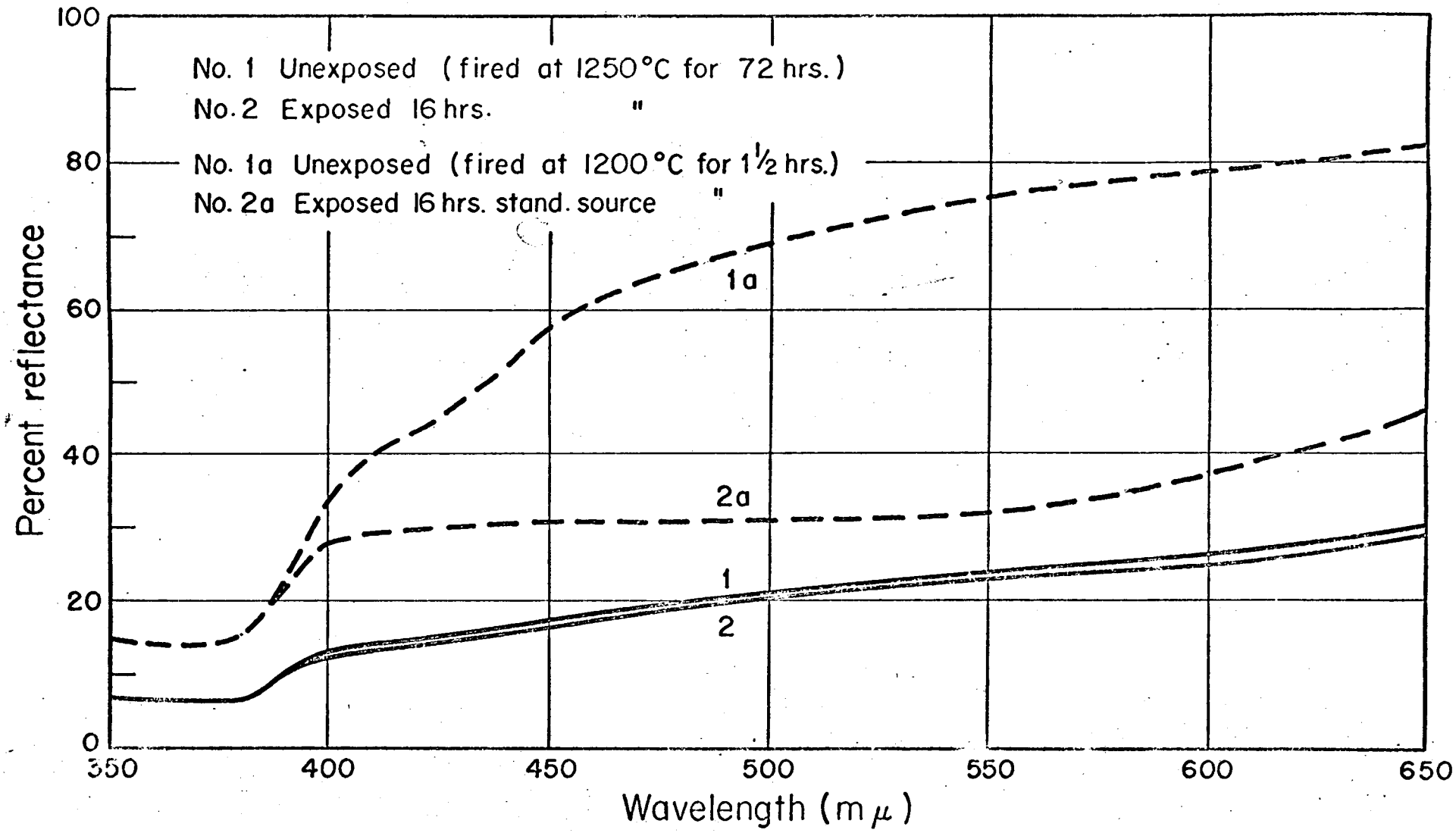

Fig. 6: $BaTiO_3$ Commercial grade lot 7C TAM Firing treatment effects on darkening curves.

the phototropic response measured by the change in reflectance upon solar irradiation is significantly decreased. It is our feeling that the reduced reflectance is due to a reduction in porosity and the associated scattering coefficients with prolonged firing. Upon prolonged firing, the pores trapped within the grains would agglomerate as has been shown in many ceramics. Pore agglomeration reduces the scattering and permits the entering light to penetrate to far greater depths within the specimens than would occur with higher scattering coefficients.

b. Kinetics of Darkening

While measuring darkening under solar irradiation and subsequent bleaching, spectral reflectances were measured after specific time intervals of exposure. This made it possible to analyze the time dependence of the reflectance change and recovery. For some of the specimens it appears that the darkening reaction exhibited simple first order kinetics. However, this has not been found to be the general case and at the moment the treatment of the kinetics of darkening and bleaching is only empirical. With commercial $BaTiO_3$, it appears that there are two relaxation times for the total darkening reaction (Figure 2). The first relaxation time is of the order of minutes and the second, the order of hours. Precise analysis of the relaxation is semi-empirical because somewhat arbitrary equilibrium values for initial reflectance and saturation darkening must be selected in order to analyze the relaxation. With two apparent relaxation times operative, a third intermediate reflectance value must be assigned or determined to

make all of the data self-consistent. The process of short relaxation time (minutes) only gives 10% reflectance change. It was noted that the high purity barium titanate also underwent darkening by a relaxation process with a time constant of the order of minutes. From this it was concluded that the commercial materials probably contained two impurities which were responsible for the phototropic reactions, one of which was present in the high purity barium titanate and the other of which was not. Because of the high reaction rate constant associated with the high purity barium titanate, it was judged that it might also exhibit bleaching at a lower temperature than did the commercial material. Consequently, the equilibrium reflectance for high purity barium titanate was measured as a function of temperature. The detailed results are given in quarterly report No. 7. At 70°C the equilibrium reflectance lies approximately half way between the fully bleached state and the fully darkened state for chemically pure barium titanate (TAM Lot No. 299). For all higher temperatures measured, that is, at 80°C, 90°C, and higher, the equilibrium reflectance curves are superimposed on the reflectance curve for the fully bleached state. From this it was concluded that whatever impurity is responsible for the phototropy in the chemically pure barium titanate conveys much more desirable bleach kinetics for potential satellite temperature control.

Because of the above conclusion that different impurities were responsible for the different kinetics observed in commercial and high purity barium titanate, various doping elements were added to high purity barium titanate to determine

whether the phototropic response could be increased with a specific impurity which would yield equilibrium reflectance recovery at a lower temperature than had been observed in the commercial materials. The first tests have been conducted with doping elements of iron, manganese, copper, and antimony which have previously been observed to cause phototropic response in both barium titanate and in pure titania. The doping was performed by aqueous solutions of soluble salts of the respective elements which were mixed in a slurry with the barium titanate. This was then dried, calcined, crushed, pressed and fired at 1100°C and at 1350°C. The amount of doping performed included 0.001 wt %, 0.01 wt % and 0.1 wt % of the respective additives.

Iron additions of .001 and .01 wt % fired at 1100°C did not change the extent or rate of darkening from that exhibited by the high purity undoped material. Upon firing to 1350°C the initial reflectance was decreased for both of these percentage additions. The absorption band introduced by the iron impurity at the UV cut-off as reported previously was similarly introduced. The extent of darkening was also increased by firing at the higher temperature. Further, the darkening reaction exhibited saturation at ten minutes which was the shortest interval of exposure employed. Thus, for the darkening reaction it appears that the iron impurity exhibits equivalent kinetics to that observed in the high purity material. The equilibrium reflectance as a function of temperature after darkening did not also exhibit identical behavior with the pure barium titanate.. Approximately 5% recovery in reflectance occurred at 60°C, and further recovery was observed with

increasing temperature though only approximately one-half of the total reflectance change was recovered at temperatures up to 175°C, which was the highest temperature measured. Similar results were obtained with the sample containing 0.1% iron though they differ in the quantitative detail. A much larger response occurred with the samples fired at 1100°C for this content of iron than for the smaller iron content. However, essentially no bleaching occurred up to 120°C. For samples fired at 1350°C, the results are shown in Figure 7. The equilibrium reflectance is decreased more than that exhibited by the barium titanate as shown by the curve marked "bleach state". The equilibrium reflectance at 30°C is decreased by approximately 20%. At successively higher temperatures the equilibrium reflectance increases, recovering approximately 10% at 100°C or half the total change in reflectance observed. Thus, the higher content of iron fired to the higher temperature tends to exhibit more recovery of reflectance at lower temperatures than do the smaller iron content specimens. Similar results were obtained with the antimony-containing specimens. The equilibrium reflectance was consistently decreased, the change in the dispersion of the UV cutoff was also observed, and the magnitude of change in reflectance was increased with each of the antimony additions. In contrast to the results obtained with iron additions, the fractional recovery upon heating to successively higher temperatures was much smaller for antimony additions than was exhibited by the iron-containing specimens. Therefore, the results are not reproduced here. Measurements on the other samples containing

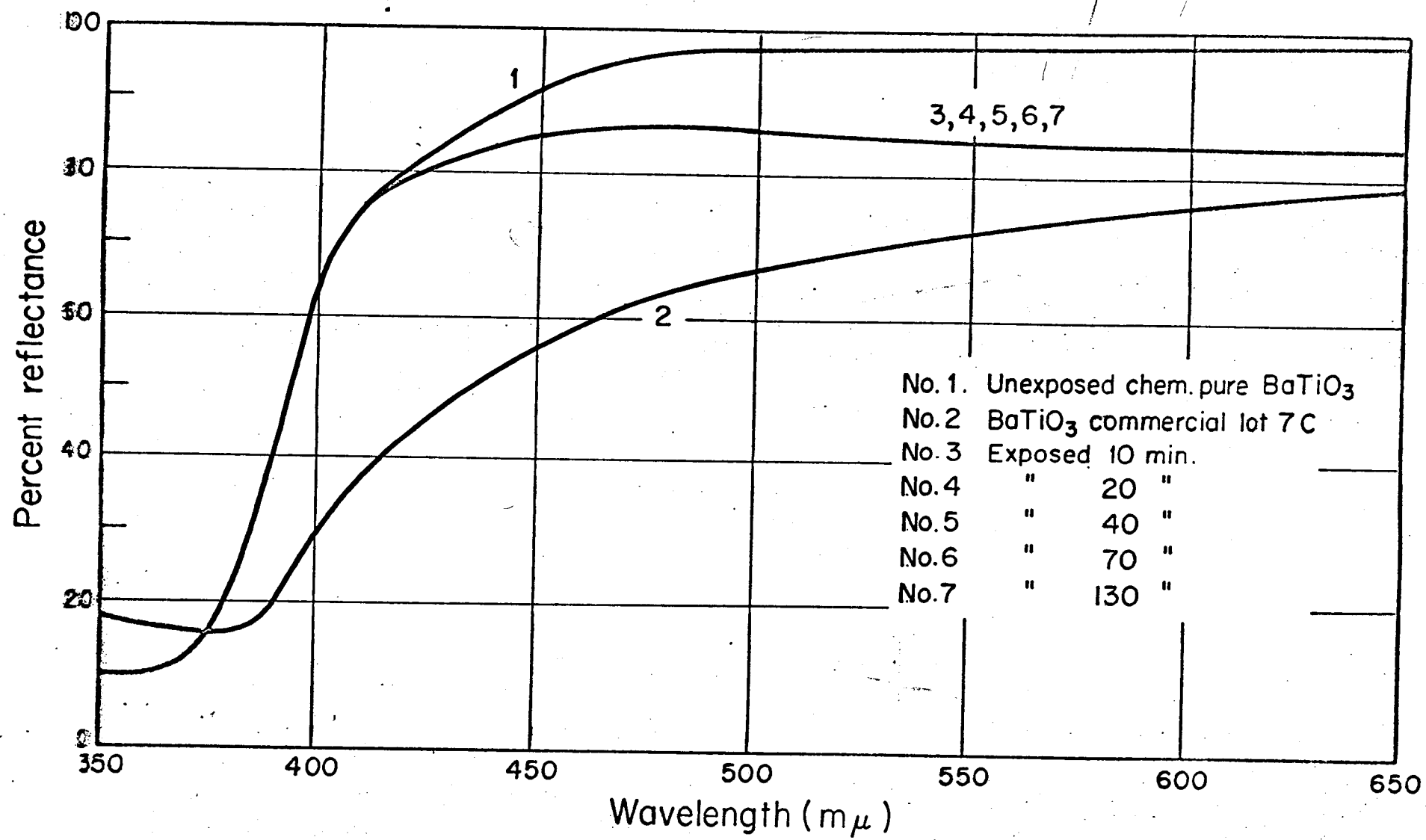

Fig. 7: Darkening curve for C.P. $BaTiO_3$ Lot 30C
TAM

doping elements have not been carried through to a state to be reproduced at this time.

c. Phototropy in other lots of Commercial Barium Titanate

In addition to the above doping experiments in high purity barium titanate in an attempt to determine which of the various impurities are responsible for the fast and large phototropic response, we also obtained other lots of barium titanate. These were formed as polycrystalline ceramic specimens and the initial reflectance, darkening rates, and equilibrium reflectance as a function of temperature were briefly examined. Lots nos. 53-C, 50-P, and 51-C all exhibited high initial reflectance and a change of 20% reflectance within 10 mins., with further darkening of approximately 10% reflectance with an additional one hour exposure. Lot no. 45-C exhibited a much lower initial reflectance and changed by approximately 10% on exposure. Lot no. 1CN exhibited a very high initial reflectance and changed by approximately 5% within 10 mins. The latter lot, 1CN appears to behave identically to high purity materials examined previously.

Examination of the chemical analyses of the various lots upon which measurements have been made reveals no significant difference between the various impurities such as iron, manganese, vanadium, or copper considered to be responsible for the phototropic reaction. The largest difference is observed with the lot designation 1CN which has a much higher barium

to titanium ratio than the other lots. Consequently, in addition to the doping elements already examined, it appears that we must also consider changing the barium to titanium ratio and observe the effects this has on phototropic response.

The above results on the effect of the impurities on the phototropy in barium titanate appear promising with respect to the determination of which impurity causes large phototropic response, fast reaction time, and low bleach temperatures. However, the observed sensitivity to firing temperature suggests that this must be further surveyed in order to characterize the effects fully. Whether the sensitivity to firing temperature is due to the time required for the impurities to enter solution or whether it is due to the additional pickup of impurities from the furnace is not now known.

d. Pure Barium Titanate

The spectral response of the initial reflectance and the darkening and bleaching for samples prepared with high purity barium titanate are not as easily reproducible as are those for commercial barium titanate. Changes in initial reflectance in the range of 10% have been observed. This may result from the fact that the control of contamination is more serious for the high purity samples than it is for the commercial samples. We have prepared far fewer high purity specimens than commercial specimens but anticipate achievement of equivalent reproducibility as with commercial grade materials.

e. Spectral Dependence of Darkening

The spectral dependence of darkening has been investigated by exposing various barium titanate samples to the standard solar source with interference filters for the UV region and Wratten filters for the visible interposed between the source and the specimen. Because the total integrated intensity is drastically reduced through these filters, we originally intended to compare the rates of darkening on the basis of equivalent irradiations. We have found that unnecessary for two reasons. First, reasonable estimates of the integrated intensity can be made from the known transmission characteristics of the filters. The transmissions measured on our spectrometer shows good agreement with the specifications. It was then possible to select the appropriate areas passed by the respective filters from the known distribution of our standard light source. A few measurements, however, revealed that the intensity effect is decidedly secondary. Darkening under the full solar irradiation and through the 335 mμ band-pass filter and a 393 mμ band-pass filter were equivalent. Thus, for these wavelengths there is sufficient energy to activate the sites which contribute to the phototropic reaction. Since the 335 mμ filter transmits significantly greater flux than the 393 mμ filter, it is surprising that the rates of darkening are not different by roughly a magnitude total flux than the standard solar source. Therefore, the discrepancy for the intensity effect on darkening in comparison with the relative fluxes is very large, and is not now

understood. We have not yet considered the implication of this with respect to potential satellite temperature control.

The rate of darkening through a blue filter which peaks at 430 mμ was drastically reduced in comparison with the rates of darkening through the UV filters or the full solar irradiation. Because the others exhibited no marked intensity effect, it is concluded that the blue filter comes very close to the cut-off or limiting energy required to activate the defects responsible for the phototropic reaction. Upon exposure through a green filter, the results were simply scattered. There was not a consistent darkening or bleaching amid the 5% scatter exhibited by the successive measurements. From this it is concluded that all of the wavelengths transmitted by the green filter are of insufficient energy to activate the sites responsible for phototropy. Since the peak transmission of the blue filter was at 430 mμ with its lower wavelength cutoff at about 400, this places the energy limit for the activating radiation at approximately 400-430 mμ.

f. Spectral Dependence of Bleaching

A commercial barium titanate sample was darkened to saturation under the full solar source. The pre-darkened sample was then irradiated through the red and green filters successively. Exposure through the red filter did not provide any bleaching. Exposure through the green filter did not provide any bleaching.

VI. MECHANISM OF PHOTOTROPY

The above results required that we modify the proposed mechanism for phototropy in barium titanate upon which our experimental program was based. It had been assumed possible for the phototropic reaction to take place by the removal of an electron from an oxygen vacancy with subsequent trapping of that electron at a titanium site changing the titanium valence from four to three. The broad band absorption change could be due to conduction within "d" shells of titanium. Alternately, with elevation of electrons from the valence band to the oxygen ion vacancy; broad absorption would be possible by conduction of the positive holes in the valence band. It is well known that reduced barium titanate contains excess anion vacancies, with an appropriate number of titanium ions changing in valence. If the broad band absorption were due to conduction through the "d" shells in the titanium, our samples given reducing heat treatment (Figure 5) should have exhibited uniform reflectance changes similar to the phototropic darkening. Instead there was only the narrow band between 390-450 millimicrons in which the reflectance was decreased with reducing treatment. The influence of impurities and particularly the interpretations that iron or manganese or antimony or vanadium are necessary additives for enhanced phototropy in barium titanate suggest that conduction through titanium "d" shell levels is not responsible for the phototropic reaction. If we assume then that the impurities introduced additional energy levels within

the band structure another possible phototropic reaction can occur by the transfer of electrons between these respective impurity levels. We had assumed earlier that the broad band absorption would take place by the subsequent elevation of electrons from donor traps into the conduction band. If the energy gap between the donor level and conduction band is small then a broad range of wavelengths in the visible region and into the infrared could be absorbed because of the lack of an upper energy boundary in the conduction band. However, that mechanism must be rejected because of the lack of bleaching of pre-darkened material upon exposure through a red filter. The peak transmission of the red filter lies at 650 millimicrons with the lower cut-off at about 600. This wavelength region is included in the broad band absorption after darkening. For the above model, exposure to the red filter should elevate electrons from the upper level donor sites. The electrons would then be free to migrate and have a certain probability of being recaptured at the low energy level from which they were activated. Because we do not observe bleaching with red irradiation suggests that this is not the most probable scheme for describing the energy levels possible for phototropic response. This would suggest then that the activating process and the subsequent trapping and the absorption which occurred after trapping takes place by a very localized interchange. That broad band absorption takes place while the electrons are localized to specific sites, and that they do not become activated into the conduction band is also inferred.

Two different sets of measurements were made related to the characterization of the defects and their localization. These consisted of conductivity measurements as a function of frequency and of low temperature reflectance in bleached and darkened states.

No photoconduction occurred during exposure to the source. This suggests that the defects responsible for phototropy are either highly localized or do not carry charge.

Reflectance measurements at liquid nitrogen temperature are equivalent to the room temperature values in both darkened and bleached states. This shows that thermal broadening has not occurred at high temperatures and that the broad band absorption observed at room temperature does not result from a thermal broadening of narrower peaks corresponding to individual defects which would be resolved at low temperatures. Thus, the low temperature measurements do not specifically indicate the presence of localized effects with sharp absorption lines associated with them.

Our objectives are: to search for a material with a high change in absorption coefficient which exhibits bleaching at lower temperatures than those which we have found to date, to fully characterize the materials for potential use, and to the mechanism of phototropy. The mechanism study is confined to the barium titanate base materials because they at present appear to be the most promising phototropes for potential satellite temperature control.

VII. CONCLUSION

The sodium chloride—silver chloride mixture found to be photosensitive offers considerable promise for satellite temperature control because of the possibility of adjusting the temperature by adjusting the composition (If the assumption is valid that the bleached temperature will occur at the two phase boundary). Further work will be done to determine whether or not this is the case.

The phototropic reaction for barium titanate is to be optimized with respect to lower temperature bleaching. This is being pursued because of the observed low temperature recovery under irradiation in high purity barium titanate. The specific impurities responsible for the phototropic response in high purity barium titanate in comparison with commercial barium titanate are being investigated with an empirical technique. The effects have been found to be sensitive to firing temperature. Further work on both other additions and firing conditions are to be covered in the next quarter. Greater phototropic response and greater recovery at low temperatures have already been found with the iron additions than we have previously observed in titanates.

In the mechanism studies, we clearly need a new model upon which to guide our experimental investigation.

REFERENCES

1. Brown, G. H. and Shaw, W. G., Reviews of Pure and App. Chem. Mar. 1961 p 2-32

2. Soshen, R. W., Pekker, A. J., and Sturtz, J. P., J. Phy. Chem. Solids, 5, No. 23, 1958

3. Lee, O. I., Amer. Mineral, 21, 764 (1936)

4. Williamson, W. O., Ceramic Age 37, No. 5, 160, (1941)

5. Waugh, A., personal communication

6. Weyl, W. A., "Colored Glasses", Soc. Glass Techn. Richard Clay & Co. Ltd., Bungay, Suffolk, (1951)

7. Eckert, F. and Schmidt, K., Glastech Ber, 10, 80, (1952)

8. Rindone, G. E., Travaux IV, Congress Int'l du Verre, Paris, (1956)

9. Brown G. and Shaw, Reviews of Pure and Appl. Chem., Mar. (1961)

10. Bushay, A., Phys & Chem. Glasses, 2, 33, (1961)