NASA SP-5014

TECHNOLOGY SURVEY

Technology Utilization Division

NASA CONTRIBUTIONS TO
THE TECHNOLOGY
OF INORGANIC COATINGS

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Washington, D. C. 1964

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Foreword

The Administrator of the National Aeronautics and Space Administration has established a technology utilization program for "the rapid dissemination of information . . . on technological developments . . . which appear to be useful for general industrial application." From a variety of sources, including NASA Research Centers and NASA contractors, space-related technology is collected and screened; and that which has potential industrial use is made generally available. Information from the nation's space program is thus made available to American industry, including the latest developments in materials, processes, products, techniques, management systems, and analytical and design procedures.

This publication is part of a series intended to provide such technical information. It reviews major NASA research in the field of inorganic protective coatings for thermal protection and lubrication purposes, and was prepared by the Denver Research Institute from data supplied by the NASA research facilities. Some NASA-sponsored work is also discussed.

THE DIRECTOR, *Technology Utilization Division*
National Aeronautics and Space Administration

ACKNOWLEDGMENTS

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TECHNOLOGY OF INORGANIC COATINGS

Introduction

The two principal objectives of this technological survey are: (1) The identification and evaluation of National Aeronautics and Space Administration (NASA) contributions to the science and technology of inorganic coatings; and, (2) The preparation of a report suitable for the dissemination of NASA contributions in a form which will assist the commercial economy.

Advanced space/missile requirements dictate the development of new combinations of materials with markedly superior properties. The sophisticated combination of two or more substances into a composite-materials system yields a combination of properties unobtainable from any single substance. An excellent example is vitreous-porcelain enamel. This composite combines the strength, flexibility, and other useful properties of the metallic substrate with the excellent chemical resistance, diversity of color and texture, ease of cleaning, etc., provided by a coating a few mils thick of bonded glass. Inorganic coatings represent an important division of composite materials systems currently undergoing rapid development to serve novel applications. The following are presented as examples of inorganic materials: glasses, crystalline ceramics, carbides, silicides, borides, sulfides, and metals.

New combinations of inorganic coatings were developed to satisfy the rigorous environment of space such as the extremes of high and low temperatures, the ultra-high vacuum (10^{-14} Torr), ultraviolet, solar-proton and cosmic-ray irradiation, and micrometeorite erosion.

This report is subdivided into seven different areas of NASA interests which in most cases broadly coincide with industrial classifications. These areas are: (1) Thermophototropic Coatings; (2) Thermal Control Coatings for Space Vehicles; (3) Solid Lubrication Coatings; (4) Thermal Insulation Coatings; (5) Methods of Applying Coatings to Substrates; (6) Measurement of Coating Optical Properties; and (7) Refractory Metal Oxidation Resistant Coatings.

The following general statements indicate the commercial implications of NASA inorganic coating developments for each area of interest: (1) thermophototropic coatings assure new optical devices whose optical properties actively respond to light intensity; (2) thermal control coatings developed for space applications may be useful for solar energy conversion systems and thermal radiation control; (3) solid lubrication coatings

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developed for high- and low-temperature space applications should lead
to the development of specialized and improved lubricants for commercial
uses; (4) thermal insulation coating concepts should assist the develop-
ment of industrial high-temperature thermal insulations; (5) parametric
studies of coating application methods have improved the coating-to-
substrate bonding; (6) devices and techniques developed by NASA for
measuring various optical properties may prove to be commercially
useful; and (7) refractory metal coatings after suitable development will
yield a new group of high-temperature structural materials.

The publication of all NASA inorganic coating contributions in this
single report is made to facilitate and to stimulate the use of develop-
ments in one area by an adjoining area. Cross fertilization of ideas,
techniques, and methods appears to be a particularly useful and fruitful
possibility in the rich and diverse (but with many common factors)
inorganic coating technology. Inorganic materials are extremely useful
in the field of microelectronic components and thin-film electronic appli-
cations. None of this information is included as this technology uses
highly specialized techniques which set them apart from the other
inorganic coatings which deal with extended-area surfaces. On this basis
some direct-energy-conversion coatings work was included, but the
complete technology of semiconductor solar cells was not discussed. In
the final analysis, a good number of these decisions are arbitrary and
reflect the author's bias, particularly in the fringe areas.

This technological survey originally was intended to include all NASA
contributions from *all* NASA Research Centers and from *all* individual
contractors, universities, and nonprofit institutes. However, after
initial interviews with personnel at the various NASA Research Centers,
it was apparent that the expected quantity of NASA contributions has
originally been underestimated. Therefore, this survey includes only
contributions from the NASA Research Centers and those from NASA
contractors or grantees having their reports available at the initial
interview. It is estimated that twice as much information would have
been available for this report if all the contractors and grantees had been
completely surveyed.

The volume of technical information currently being generated within
an organization the size of NASA justifies the present survey in bringing
together information distributed through numerous documents.

A number of general references are available which cover in detail
particular topics relating to inorganic coatings. Huminik (ref. 1) recently
considered the field of high-temperature coatings; and Powell, Campbell,
and Gonser (ref. 2) presented the state-of-the-technology of chemical
vapor deposition. Inorganic coatings developed especially for lubrication
purposes are comprehensively and authoritatively treated by Bisson and
Anderson (ref. 3).

During the studies on inorganic coatings it became evident that NASA contributions have technical possibilities in commercial applications. However, their adoption by commercial firms will be influenced by a detailed cost and/or profit evaluation. Since most firms consider this type of information as proprietary, the author takes the position that the function of this report is to stress the probable technical *implications* rather than *applications*. Thus, it remains for various commercial firms to evaluate this report as to its usefulness for specific purposes.

Welles, Marts, Waterman, Gilmore, and Venuti (ref. 4) present a good treatment of the nature and extent of the commercial application of missile/space technology.

Sufficient time was not available during the preparation of this report to permit reflection and analysis of the commercial implications. Consequently the author chose to present as much information as possible and to offer as examples only those commercial implications which were readily apparent.

Thermophototropic Coatings

THERMOPHOTOTROPY

Scientific interest in the interaction of materials with photons, particularly as it affects the optical absorption properties of solids, dates from 1870 when Orr (ref. 1) observed the darkening of lithopone paint. Phipson (ref. 2) noted the same unusual effect on the paint used on a gate post, but did not reach an understanding of the phenomenon. In general, the technical and scientific interest in the effect of light on darkening or bleaching the color of solids has primarily followed the direction of Cawley (ref. 3) in preparing more stable solids.

A lack of significant interest in the effects produced by the interaction of light, materials, and temperature has occasioned a numerous and conflicting terminology. The following definitions are based on a review of other published definitions:

1. Thermophototropism is the temperature-dependent alteration of optical absorption of a material when exposed to light of particular wavelength distributions.

2. Phototropism is the phenomenon associated with the reversible change in optical absorption of a material when exposed to light of a particular wavelength distribution, which reverts to its initial absorption at room temperature when the illumination is terminated.

3. Thermochromism is the phenomenon associated with the reversible-temperature alteration of the optical absorption of a material.

Thermophototropism is a quite general phenomenon with respect to temperature; while phototropism is a special case that applies to room temperature reversibility. Both thermophototropic and phototropic materials have some lower temperature limits at which the darkened state can be "frozen-in," but differ in that the latter reverts to its original state in the absence of illumination at room temperature, while the former possesses a reversal temperature. Because the distinction appears

trivial, it is suggested that the use of the terms phototropism or photo-tropic should be discontinued.

A clear distinction must be made between thermophototropism and thermochromism. Thermochromism is simply temperature-dependent optical absorptivity, and is not a function of illumination effect as is thermophototropism. Further distinctions must be made between the optical processes which absorb energy and re-emit photons. For example, phosphorescence and fluorescence, or the release of energy of trapped photoelectrons (thermoluminescence) must be differentiated from thermophototropism or thermochromism.

On the basis of the definition it is possible to construct a general model for the thermophototropic process, but not to detail the exact mechanisms for particular systems. Figure 1 shows the energy levels associated with one simple model of thermophototropy. When the material is exposed to a light quanta possessing energy equal to or greater than $(h\nu)$, photo-excitation takes place and generates a given number of photoelectrons,

$\Delta E_a = h\nu$

$N_a = \phi N h\nu$

$N_b = A \exp \dfrac{\Delta E_b}{RT}$
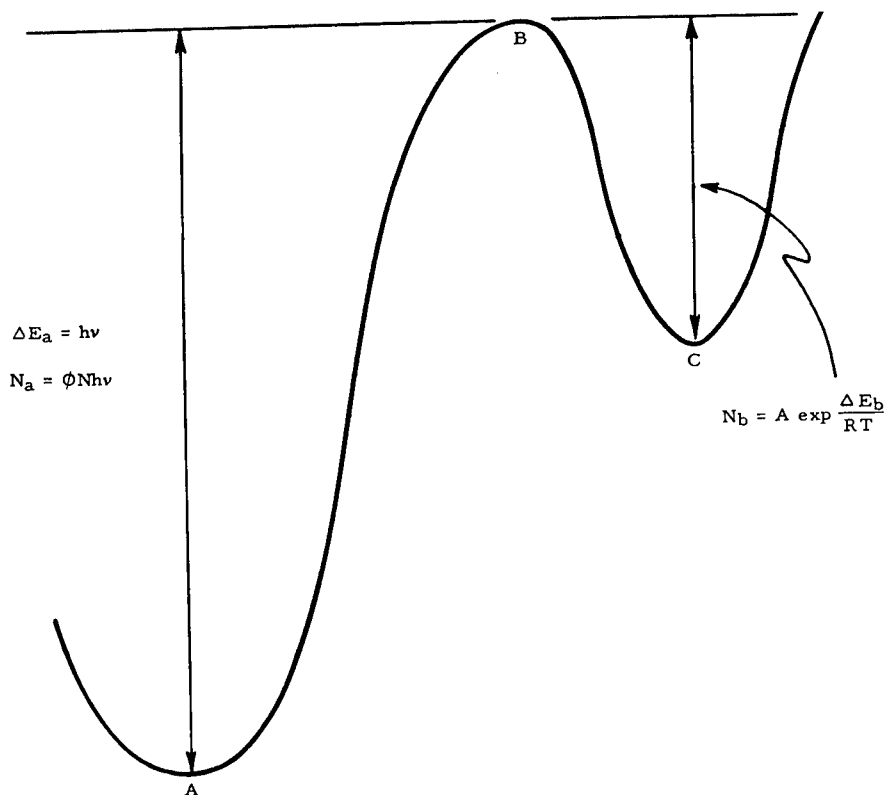
FIGURE 1.—General model of thermophototropy.

depending upon the quantum efficiency of the process, some of which are trapped in metastable energy levels. Metastable photoelectrons may be thermally activated over the energy barrier with an activation energy (ΔH).

Because the photoelectrons are trapped in energy sites above the stable states, less energy is required to excite them, and the absorption band associated with these color centers lies at a longer wavelength (i.e., $(\Delta E)_a > (\Delta E)_b$). Depending upon the specifics of the situation, optical bleaching of darkened material may not occur if the quantum efficiency is low. In this case, the photon energy absorbed at the longer wavelength is dissipated to the lattice as heat.

Inorganic and organic, solid and liquid thermophototropes have been classified by one or more of the recent bibliographies (ref. 4) or reviews (ref. 5). We shall focus our attention on the inorganic materials. A large number of oxides containing small amounts of impurities have been found to be thermophototropic (ref. 6), as shown in table 1, but the most interesting, because of the large color changes, are the titanates and titania. McTaggart and Bear (ref. 7) investigated rutile and anatase structures and concluded that only rutile exhibited thermophototropic behavior. However, since a large number of doping ions produced noticeable optical activity (tables 1 and 2), with the greatest color change (yellow to black) being associated with Cr_2O_3 additions, they concluded that oxygen vacancies were created in the surface of the crystals adjacent to adsorbed doping materials, and that the presence of oxygen and water vapor at the reacting surface was essential to the reaction.

Takei (ref. 8) investigated the mercury compounds of the $HgX_2 \cdot 2HgS$ and $HgXCNS \cdot 2HgS$ types, where X represents a halogen ion. In table 3, Schutt (ref. 9) lists the thermophototropes which appear most useful for space-temperature-control application. Presently, the bleaching-temperatures are too high or the compounds quickly become irreversible upon extended exposure to sunlight. Takei attributes the optical behavior to a phase change in the compounds. However, it appears that the detailed mechanism of thermophototropy in these mercury compounds is unknown.

The significant area of research in the thermophototropic phenomena of inorganic compounds is the elucidation of mechanism in particular materials. Progress cannot be made without quantitative measurements of optical, electrical, magnetic, and chemical parameters. Single crystal experiments will be useful for those systems in which the optical activity is a bulk property, but it is not clear that any materials are of this type. Without doubt the model used in this discussion is a simple, direct one, and investigators must detail the complicating secondary reactions peculiar to each material.

TABLE 1.—*A Comparison of Absorptivity Changes for Acidic and Acidic-Basic Impurity Introduction for* $BaTiO_3$

Sample (mole %)	400 $m\mu$	500 $m\mu$	600 $m\mu$	700 $m\mu$
V^{+5} (.02)	0	2	1	1
V^{+5} (.02)+$NaOH$(10)	17	56	49	39
Cr^{+3}(.02)	0	2	1	1
Cr^{+3} (.02)+$NaOH$(10)	21	55	54	41
Mn^{+3-4}(.02)	0	½	½	1
Mn^{+3-4}(.02+$NaOH$(10)	8	26	32	30
Fe^{+3}(.02)	1	6	4	3
Fe^{+3}(.02)+$NaOH$(10)	10	46	53	48
Co^{+2}(.02)	6	4	4	3
Co^{+2}(.02)+$NaOH$(10)	6	10	16	25
Ni^{+2}(.02)	0	2	2	1
Ni^{+2}(.02)+$NaOH$(10)	23	57	57	50
Cu^{+2}(.02)	2	8	4	0
Cu^{+2}(.02)+$NaOH$(10)	10	41	47	40
Zn^{+2}(.02)	0	6	5	4
Zn^{+2}(.02)+$NaOH$(10)	11	44	45	33

TABLE 2.—*Effect of Na Concentration on the Absorptivity of Impure* $BaTiO_3$

Na (conc.)—mole %	Absorptivity increments (%)			
	400 $m\mu$	500 $m\mu$	600 $m\mu$	700 $m\mu$
2	6	30	26	17
5	9	50	47	36
10	15	50	49	37
15	9	55	52	37
20	9	52	51	37
30	8	48	47	35

TABLE 3.—*Absorptivity Changes (%) for Impure* $CaTiO_3$–Na_2O *and* $SrTiO_3$–Na_2O *Systems*

Sample	$CaTiO_3$				$SrTiO_3$			
	400 $m\mu$	500 $m\mu$	600 $m\mu$	700 $m\mu$	400 $m\mu$	500 $m\mu$	600 $m\mu$	700 $m\mu$
Na	8	25	26	23	10	17	14	9
K	6	21	19	14	13	18	15	10
Li	--	--	--	--	9	13	11	8
Impure	6	13	13	9	19	17	14	8

NASA CONTRIBUTIONS

During February, 1959, an investigation was made of titania and titanates suitable for application as ceramic pigments by Plunkett and

Iwaszko of the O. Hommel Company of Pittsburgh. They unexpectedly observed thermophototropism in rutile doped with 0.5 percent RuO_2. Initial qualitative tests performed using a hot plate and a sample exposed to sunlight indicated that in principle the thermophototropic phenomena could be utilized as an active solid-state temperature-control coating for space vehicles. Samples were exhibited to Mr. Milton Schach of the Thermal Control Section, Goddard Space Flight Center.

Since then NASA has pursued the development of thermophototropic materials on a modest scale with considerable results. While NASA's efforts have not yielded a useful spacecraft coating, various materials have been studied and quantitative results are becoming available. A phenomenological model of thermophototropism has been developed, and basic investigations undertaken to elucidate the fundamental mechanisms involved.

A PHENOMENOLOGICAL MODEL OF THERMOPHOTOTROPISM

Schutt (ref. 9) of the NASA Goddard Space Flight Center, has derived and solved a partial differential equation which quantitatively describes the time, temperature, and thickness dependence of the absorptive properties of thermophototropic materials. This mathematical formalism is useful in describing the photoresponse of this class of materials, and has application to the thermal analysis of systems utilizing thermophototropes for temperature control.

Schutt divided the thermal dependence of the absorptivity of any thermophototropic layer into four temperature regimes: (1) above the temperature $(T\mu)$, darkening is impossible; (2) below the temperature (T_o), the absorptivity of a darkened sample adiabatically cooled is "frozen in"; (3) between the temperature (T_o) and (T_c), the rate of darkening $(\partial a/dT)$ must be positive due to a synergistic effect of temperature and photon flux in producing the enhancement of the darkening ability of a given sample; and, (4) between the temperatures (T_c) and $(T\mu)$, the rate of darkening $(\partial a/\partial T)$ with increasing temperature has a negative value. Obviously (T_c) is the temperature at which $(\partial a/\partial T)$ is zero and the absorptivity (a_M) is a maximum.

The absorptivity of any layer of a thermophototrope at a given uniform temperature, thickness, and time when exposed to constant illumination intensity and spectral distribution is given as follows:

$$a = a_o + (a_m - a_o)\left(\frac{t}{tm}\right)\exp$$

$$-\left[\left(\frac{t - t_m}{t_m}\right) + \left(\frac{T - T_c}{t_m}\right) + \eta(x - x_o)\right] \quad (1)$$

where:

a = absorptivity at wavelengths less than the critical value
a_o = minimum absorptivity
a_m = maximum absorptivity
t = time exposed to illumination
t_m = time to attain maximum absorptivity
T = temperature
T_c = temperature between (T_o) and $(T\mu)$ at which $(\partial a/\partial T) = 0$
T_o = maximum temperature at which absorptivity above the mini-
mum value is "frozen in"
$T\mu$ = minimum temperature at which absorptivity changes are not
possible
X = thickness of layer from the surface (X_o)
η = absorption index

The thermal response must be included because darkening is dependent upon the response of the material to any temperature change which occurs as a result of illumination and is approximately equal to:

$$\tau = \frac{\gamma I a_o (1 - B_V)}{mC_p} + \frac{I a_o (1 - \gamma)}{mC_p} - \frac{\epsilon \sigma T^4}{mC_p} \qquad (2)$$

where:

m = mass of the sample
C_p = heat capacity at constant pressure
γ = fraction of illumination responsible for phototropic change in
sample
B_V = quantum efficiency of the wavelength bond in the neighborhood
of the critical wavelength
I = illumination intensity
ϵ = emissivity of sample
σ = Boltzmann constant
τ = thermal response

After termination of exposure to a given illumination at a specific temperature, an absorptivity intermediate between (a_o) and (a_M) is produced. The resultant decay of darkening is given by the following relation by Schutt:

$$a = a_o + (a_M - a_o) \left\{ \frac{T_\xi}{t_M} \exp - \left[\left(\frac{t_\xi - t_M}{t_M} \right) + \left(\frac{T_\xi - T_c}{t_n} \right) \right. \right.$$

$$\left. - \frac{T_\xi - T_c}{(t_o - t_\xi)} + n(X_\xi - X_o) - n_\xi (X_\xi - X_o) \right] \right\}$$

$$\cdot \exp - \left[\frac{t - t_\xi}{t_o - t_\xi} + \frac{T - T_c}{\tau_\xi (t_o - t_\xi)} + n_\xi (X - X_o) \right] \qquad (3)$$

where:

t_ξ = exposure time

δ_1 = relative time required for the absorptivity to decay to the eth part at a given (T) and (X)

$$\delta_1 = \frac{1}{t_o - t}$$

$$\tau_\xi = \frac{T - T_c}{t_o - t}$$

$$n_\xi = \frac{1}{X_\xi - X_o}$$

The latter two terms identify the decay of their respective parts of the exponential at a given temperature and depth defined by the eth part of their contributions. The upper bound on the temperature Tu lets $X_\xi = X_o$, $t = t_M$, and $T = Tu$; therefore,

$$T_u = n\tau\, t_M + T_c \qquad (4)$$

where n is the eth part to be taken and T_u has been defined in a similar manner.

While this mathematical formalism does not allow the calculation of parameters from first principles, it does allow variations of absorptivity to be expressed as a function of the experimental parameters $a_o, a_M, t_M, T_c, T_o, \tau,$ and n. The absorptivity values are determined by spectrophotometric measurements after correcting for the beam intensity. The values of t_M and T_c must be found simultaneously by trial, and may be checked by the following relationship:

$$d(t - t_M) = -\frac{d(T - T_c)}{\tau} = \frac{d(X - X_o)}{u} = \frac{d(a - a_o)}{\left(-u + \dfrac{1}{\tau}\right)\left(a - a_o\right)} \qquad (5)$$

where (μ) the velocity at which the lowest measurable darkening level progresses through the material of thickness (L) in the time (t_L) is given by:

$$\mu = L/t_L \qquad (6)$$

Values of (T_o) and $(T\mu)$ are obtained by simultaneous illumination and heating of a given sample. The value of (τ) is obtained from the equation previously given, after B_V is obtained from optical measurements. The value of (η) is defined once (B_V) is known and $(\bar{\eta})$ has been evaluated by optical transmission measurements.

Using data provided by Lexington Laboratories, Inc., Dr. Schutt found reasonably good agreement between the theoretically-derived curve and experimental results for the 550 mμ absorptivity for barium titanate. These results are shown in figure 2.
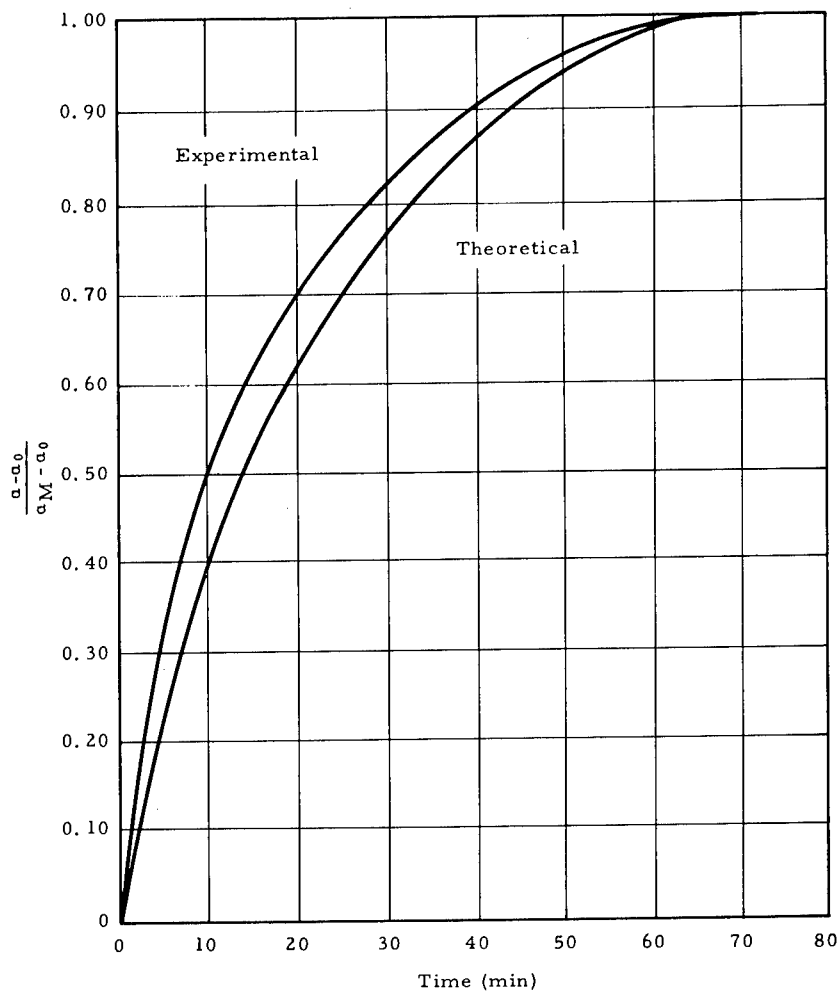
FIGURE 2.—A comparison of theoretical and experimental incremental absorptivity curves for barium titanate at 550 $m\mu$.

ENHANCED THERMOPHOTOTROPIC RESPONSE OF ALKALINE EARTH TITANATES

Schutt, Colony, and Lepp (ref. 10) have investigated the effect of acidic to basic impurity introduction on the enhanced thermophototropic behavior of alkaline earth titanates prepared from a high-purity synthesized material. In addition, quantitative measurements were presented for the enhanced photoactive titanates. Prior work consisted mainly of only qualitative observations.

Titanates were synthesized via the following oxalate process:

$$TiCl_4 + H_2O \rightarrow TiOCl_2 + 2HCl$$
$$TiOCl_2 + BaCl_2 \rightarrow Ba(TiO)Cl_4$$
$$Ba(TiO)Cl_4 + 2(NH_4)_2 C_2O_4 + H_2O \rightarrow Ba(TiO)(C_2O_4)_2 \cdot H_2O + 4NH_4Cl$$
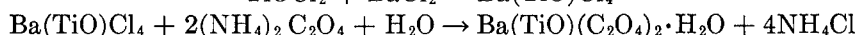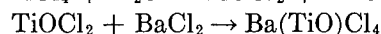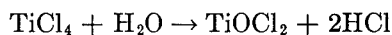
The hydrated titanyl oxalate was slurried with 0.02 mole percent $VOCl_3$, $CrCl_3$, $FeCl_3$, $NiCl_3$, $CuCl_2$ and $ZnCl_2$ and fired at 1,100° C for 4 hours to produce the titanates. After firing, samples of titanates were reslurried separately with solutions of elements in the first transition series. In an effort to identify synergistic effects due to the simultaneous replacement of titanium and barium with cations carrying different ionic charges, alkali metals were added by reslurrying the doped sample with 10 mole percent sodium hydroxide. Table 1 gives a comparison of impurity-photoactivity in an acidic titanate with that of a basic titanate. Reflectances of unexposed samples were measured and compared to a sample previously exposed to a mercury lamp for 24 hours.

The optimum concentration of sodium in barium titanate was established by varying the concentration of sodium from 2 to 30 mole percent. The reflectance changes for samples fired for 1 hour at 1,100° C are presented in table 2, and show the optimum to be 10 percent. Optimum firing conditions were 3 hours at 950° C or 1 hour at 1,100° C. Using these optimum conditions for the sodium addition to $BaTiO_3$, lithium and potassium additions were made. Although potassium-doped samples colored more rapidly, their total reflectance change was similar to that found with sodium additions. Lithium gave a smaller reflectance change.

Hydroxides of lithium, potassium and sodium were added to calcium and strontium titanates with the previously described impurities. The results, given in table 3, show that sodium and potassium increased the overall photoactivity in calcium, strontium was unaffected, and lithium yielded an inhibiting effect.

In general, Schutt, et al., concluded that the additions of sodium and potassium ions to impure barium titanate enhanced the phototropic effect in barium titanate and to a lesser extent in calcium titanate, but left strontium titanate unaffected. Since the additions were large it was assumed that the alkali metal ions are primarily surface-active and do not enter internal lattice positions. Sodium added in the carbonate form enhanced the photoactivity of barium titanate when compared with hydroxide additions as clearly shown in figure 3. The added enhancement is attributed to a lack of complete carbonate decomposition providing a "dense electron environment."

THERMOPHOTOTROPIC STUDIES OF CERAMIC GRADE TITANATE MATERIALS

Lexington Laboratories, Inc., supported by NASA Contract NAS 5-582, investigated the effect of the following parameters upon the
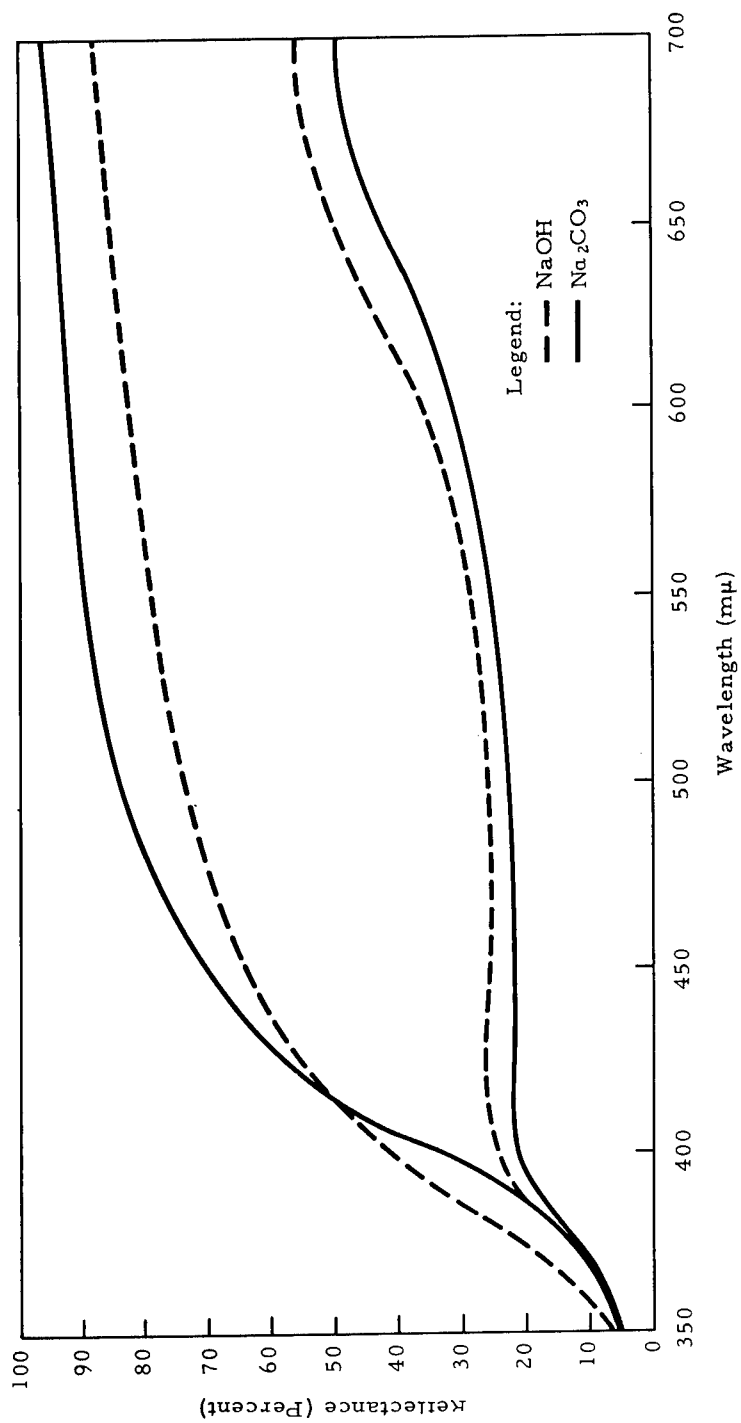
FIGURE 3.—A comparison of colorants of impure barium titanate with 10 mole percent sodium added as hydroxide and carbonate.

thermophototropic behavior of ceramic grade barium titanate (BaTiO$_3$) (ref. 11).

1. Effect of oxygen pressure on the thermophototropic properties

2. Feasibility of applying BaTiO$_3$ coatings by flame-spray techniques

3. Effect of flame-spray applications on the thermophototropic response

4. Electron-spin resonance data for darkened and bleached BaTiO$_3$.

The effect of oxygen pressure on the thermophototropic response of barium titanate was studied over the oxygen pressure range of 10 atm to 10^{-10} Torr. When using different lots of commercial material, some samples gave a moderate response as compared with the results of Schutt, Colony, and Lepp (ref. 10), while other samples showed almost no optical activity. The effect of oxygen pressure is neither clear nor consistent. Barium titanate from one particular lot exhibited optical activity in vacuum, while another lot was seriously affected by reduced oxygen pressure. Samples of barium titanate were also fired for 1.5 hours in 10 atm of oxygen, 90–300μ vacuum, and in air, subsequently these were tested in vacuum. Equally ambiguous results were obtained as before.

The thermoluminescence of capacitor-grade barium titanate was looked for, but not found, by darkening a sample in ambient atmosphere then immediately placing it in a thermoluminescence apparatus for test. A sample heated at 10° C/min to a maximum temperature of 540° C exhibited no measurable thermoluminescence, but the sample did bleach during heating.

A powder-flame-spray gun (Metco, Inc.) was used to hot-spray barium titanate powder (purity unspecified, Metco, Inc.) onto stainless steel and aluminum substrates. A second sample of known higher response was sintered, ground, and hot sprayed. As a standard of comparison, a third specimen was pressed into a pellet, sintered, and exposed with the sprayed material. A 65 percent decrease in reflectance of the Metco powder was observed, and about an 85 percent reduction in optical activity occurred with the higher response material as a result of the hot spraying.

The correlation between the phototropic behavior of sintered barium titanate subjected to different preparative treatments and the electron parametric resonance (EPR) was determined. Evidence of an (EPR) absorption signal in irradiated samples coupled with its absence in unirradiated specimens strongly supports the hypothesis that the color change is associated with chemical changes yielding unpaired electrons in the structure. Samples of fired and unfired technical grade BaTiO$_3$ were measured in the darkened and bleached state. Even though the modulation amplitude and high microwave power were used, no difference was detectable in (EPR) signals. It is, therefore, reported that no free electrons exist in the darkened state.

COMMERCIAL IMPLICATIONS

If materials possessing the required temperature and illumination-intensity characteristics can be developed, a number of important commercial applications are obvious.   For example, variable transmission car windshields, sunglasses, and windows for buildings, as well as roofing materials or self-controlled solar energy collection surfaces would all be useful devices.   Although documentation is unavailable, it is understood that a doll was marketed some years ago which would "sun-tan" when exposed to sunlight due to the use of a thermophototropic pigment.

The current commercial interest in this field is intense, though there are but few published papers originating from commercial firms. However, we are certain from private contacts that the lack of published information is actually an important indicator of the great commercial interest and not an index of disinterest.   Obviously the uses and value of glass as an optical material would be greatly enhanced by the development of compatible thermophototropic coatings or dispersions.

Cohen and Smith (ref. 12) of Pittsburgh Plate Glass described a variable transmission soda-silica ($Na_2O \cdot 2.5SiO_2$) glass doped with 100 ppm europium or the proper amount of cerium exhibited absorption bands at 3,325Å and 3,150Å, respectively.   Metastable photoelectrons were
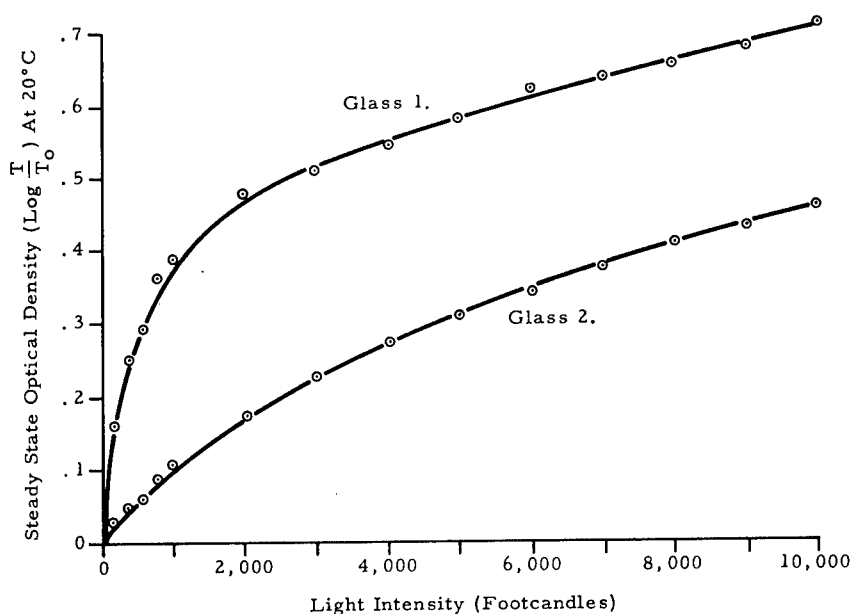
FIGURE 4.—Equilibrium optical density (D_E) versus illumination intensity (I) for two different glasses at 20° C.
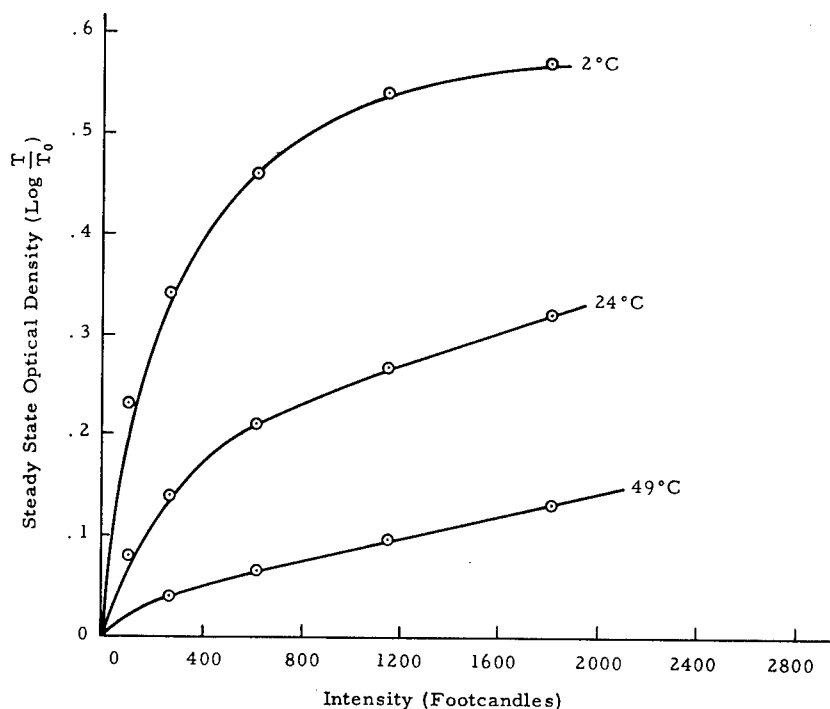
FIGURE 5.—Equilibrium optical density (D_E) versus illumination intensity (I) at three different temperatures.

trapped and produced color centers yielding a wide absorption band at 5,700Å. Twenty hours exposure to a 3,660Å light source resulted in complete decay of the color center band. Exposure to a 2,537Å light source restored the sensitivity of material. It appears that this material has a limited commercial application.

Recently, Dr. Stookey (ref. 13) of Corning Glass Works announced the development of a thermophototropic glass which is transparent when unexposed, but alters to a dark gray or gray brown upon exposure to light. Glasses containing silver chloride, silver chloride plus silver bromide, and silver chloride plus silver iodide colloidal particles are sensitive to light with 3,000 to 4,000Å, 3,000 to 5,500Å, and 3,000 to 6,500Å, respectively. These materials are subject to optical bleaching by the absorption of longer wavelength light. The steady-state optical density is given at 20° C and as a function of light intensity in figure 4. The temperature dependence is shown in figure 5. Based upon this data, it would appear that this glass has direct commercial applications, though none have been announced to date.

Even though NASA contributions to thermophototropic-coating materials have not yet resulted in commercial applications, their effects on the general technology are important. This statement is confirmed by the great interest exhibited by the public even though NASA's work is not yet generally available.

Thermal Control Coatings for Space Vehicles

GENERAL TECHNOLOGY

The temperature of a space vehicle in orbit, according to Heller (ref. 1), is a function of the following parameters:

1. Orbital characteristics.

2. Optical properties of external and internal surfaces.

3. The attitude of the momentum vector of a spinning nonspherical satellite to the direction of the sun.

4. The attitude of the spin axis to the direction of the sun.

5. The attitude of the satellite and attitude of the momentum vector to the center of the earth.

6. Heat capacity of the skin and of the instruments.

7. Conductive and radiative heat transfer between skin and instruments, and between parts of the skin (convective heat transfer is usually excluded by allowing the air to escape).

8. Internal heat release of instruments.

9. Aerodynamic heating for satellites with a perigee of less than 200 miles.

10. Environmental conditions, such as solar-constant, albedo, earth-radiation.

Internal heat transfer in a space vehicle is maximized by using high-emittance coatings and, conversely, is reduced by applying low-emittance surface coatings. The energy balance, neglecting numerous orbital parameters and internal energy generation at the external surface of a body in space in a near earth orbit, is expressed, according to Hass, et al. (ref. 2), by the following equation:

$$P_s\, \alpha + P_a \alpha + P_e \epsilon - A\sigma\epsilon T^4 = mc(dT/dt)$$

where:

P_s = Direct solar radiation incident upon the body

P_a = Earth-reflected solar radiation upon the body

P_e = Earth-emitted radiation incident upon the body

α = Solar-absorptivity of external body surface

ϵ = Hemispherical-emittance of external body surface and assumed to be equal to the absorptance of the earth emitted radiation

A = Surface area of shell
σ = Boltzmann constant
T = Body surface temperature
m = Mass of body surface
t = Time

The ratio of P_s, P_a, and P_e is a function of the orbital parameters and the time of launch, which fix the amount of sunlight, etc., received during a specified time period. Assuming that equilibrium is attained when $mc \, dT/dt = 0$, and by solving for the average equilibrium surface temperature, we obtain:

$$T = \sqrt{\frac{(\alpha/\epsilon)(P_s + P_a) + P_e}{A\sigma}}$$

Thus, the optical properties which can be altered to provide specified equilibrium temperatures of space vehicles are (α) and (ϵ) or more exactly, not their absolute values but, the (α/ϵ) ratio. This is a very simplified model; more detailed mathematical frameworks and exact analytical procedures relating to nonspherical satellites under different launch conditions are given by Heller (ref. 1), Thostesen, Hibbs, and Buwalda (ref. 3); and Camack and Edwards (ref. 4).

Before discussing particular coatings, their (α/ϵ) ratios, and their equilibrium service temperatures, we shall review briefly the range of space vehicle temperatures desired from the more important points of view. Unmanned space vehicles which do not carry electronic apparatus and are inert and silent, generally require rudimentary temperature control coatings. For example, Explorer IX was an inflated rigid satellite that could withstand a wide range of temperatures; the main limitation was the maximum temperature imposed by the strength reduction above 100° C of the plastic-aluminum foil laminate. Other inflatable space vehicles, Echo I and Echo II, must specify lower limits of allowable temperature required to maintain the internal pressure produced by sublimating solids.

Unmanned satellites containing electronic apparatus must keep their temperatures within −10° C and +100° C as the outer limits. Most transistors are useful from 0° C to +60° C, and chemical batteries lose rated power output rapidly below 10° C, though the conversion efficiency of silicon solar cells increases with decreasing temperature. The general reliability of resistors, capacitors, relays, transistors, and chemical batteries decreases with temperature increases above 20° C. Thus, for electronic apparatus, the most suitable temperature range is 20 to 40° C.

For manned or biological space vehicles, the temperature range allowable is further reduced. Manned spacecraft must not exceed 110° F for periods longer than a few minutes. In some cases, as for example, the

study of biological reproductive processes in space, a total temperature range of less than a few tenths of a degree is desirable.   In general, the technology of temperature control coating is growing at a swift pace, but the requirements for specialized surfaces are probably growing more rapidly.

To achieve a specified temperature, two different approaches are used: (1) passive coatings, and (2) active systems.   Active systems in theory provide a much closer temperature control, but they usually require additional power and weight which is a space luxury.   Several solid-state, active temperature control coatings are under development; however, this report will discuss only one possibility, thermophototropic coatings.

Active or self-regulating coatings are greatly needed to accommodate changes in thermal energy density which occur during flights of close-in, solar, and planetary probes.   The successful flight of Mariner II to Venus came perilously close to failure due to improper temperature control. The most common and currently successful active type system is a mechanical contrivance consisting of a set of shutters connected to a thermostat.   When the temperature is too low, the high (α/ϵ) surface is presented to the sun and when the temperature is too high the shutters move to expose a low (α/ϵ) surface.   Active mechanical systems will not be discussed; however, suitable coatings required for their surfaces will be mentioned.

If the shutters are to be as efficient as possible, the high α/ϵ side must have the highest possible value of α and the low α/ϵ side must have the highest possible value of ϵ.   In other words, a polished metal surface even though having a high α/ϵ would nevertheless be a very inefficient shutter surface due to the low value of α.   The consequent necessity of oversizing the active area would generally be undesirable.

In general, polished metals exhibit a higher absorptance in the shorter wavelength region (less than $3.0\,\mu$) where most of the solar radiant energy occurs, and a low emissivity in the 8 to $25\,\mu$ region which is the wavelength spectrum of most importance to a $300°$ K emitter, such as a typical satellite.   Thus, metals, and particularly polished metals, show high (α/ϵ) ratios, and in general provide equilibrium temperatures that are too high. Ionic solids, such as oxides of nontransition elements, MgO, Al_2O_3, SiO_2, ZrO_2, etc., interact at wavelengths shorter than about 0.3μ by photon-electron interaction, and at wavelengths of 6μ to 8μ by photon-ion interactions.   Since no interaction processes occur within the major portion of the solar emission region, a low solar absorptivity is typical of these materials.   On the other hand, the photon-ion interactions are efficient absorbers and emitters; consequently, nontransition ionic solids generally have low (α/ϵ) ratios.

The following technological survey of temperature control coatings is

TABLE 4.—*Methods of Obtaining Various Types of Surfaces*

Optical type of surface	α_s	ϵ_T	Polished metals	"As Received" metals	"Sandblasted" metals	Vacuum metallics	Vacuum nonmetallics	Conversion coatings	Plated coatings	Metallic paints	Nonmetallic paints	Vitreous enamel	Inorganic bonded	Transparent conversion	Transparent nonpigmented paints
Total Absorber	.9	.9						X			X	X	X	X	X
Median I.R. Absorber	.9	.5					X	X						X	X
Solar Absorber	.9	.1				X	X		X						
Median Solar Absorber	.5	.9			X			X			X	X	X	X	X
Medium	.5	.5		X	X		X	X		X			X	X	X
Median Solar Absorber	.5	.1	X			X	X		X						
Solar Reflector	.1	.9						X			X	X	X	X	X
Median I.R. Reflector	.1	.5		X			X	X		X				X	X
Total Reflector	.1	.1	X			X	X		X						

taken in large part from the recent paper of Snoddy and Miller (ref. 5). Table 4 shows the range of values of solar absorptance and emittance properties divided into several subcategories that can be obtained through the selection of different materials and processes. The properties of metals, thin films, and pigmented systems for ultraviolet exposure, light weight, electrical conduction, availability in large surface areas, prelaunch stability or repairability, and ascent stable are given in general terms in table 5.

Figure 6 indicates the location of various types of temperature control surfaces and their regions when plotted on a graph of (α) versus (ϵ). The numbers at the ends of the lines give: (1) (α/ϵ) ratios; (2) the temperatures of an insulated flat plate; and, (3) the temperature of an isothermal sphere at 1 A.U. (mean distance from the sun to earth). For different applications it frequently is not only necessary to specify the (α/ϵ) ratio, but also the absolute value of one of the optical parameters. For example, in the early days of satellite launching, tracking networks were inadequate and many experiments depended upon optical or visual observations (Operation Moon Watch). Obviously, for maximum visibility, either a high solar reflectivity or a low adsorptivity (α) was required.

To provide a space vehicle designed with the greatest flexibility, complete coverage of the area within figure 6 is highly desirable. Snoddy and Miller presented a series of figures which clearly indicate the regions for which surfaces, coated and uncoated are currently available. Figure 7 indicates the overall situation. Currently the most seriously needed coatings not now available are those which lie in the region of low solar absorptance and low (α/ϵ) ratios. Secondary requirements often imposed on the thermal control surface were mainly ignored in the construction of this figure. The effects that such additional requirements have on the availability of surfaces are shown in the following figures. Figure 8 gives currently available ultraviolet-stable coatings, and it is to be noted that the area previously mentioned as being of critical current interest has expanded. Likewise in figure 9 the availability of thin, electrically-conducting surfaces is even more limited in all (α/ϵ) values less than unity. The present large surface coatings are very limited but fortunately those available lie in one of the most critical regions where (α/ϵ) is near unity (fig. 10). Repairable or prelaunch, ascent-stable surfaces are indicated in figure 11.

The following discussion of different types of surfaces, taken directly from Snoddy and Miller, is recent and authoritative. No similar summary of equal completeness is available.
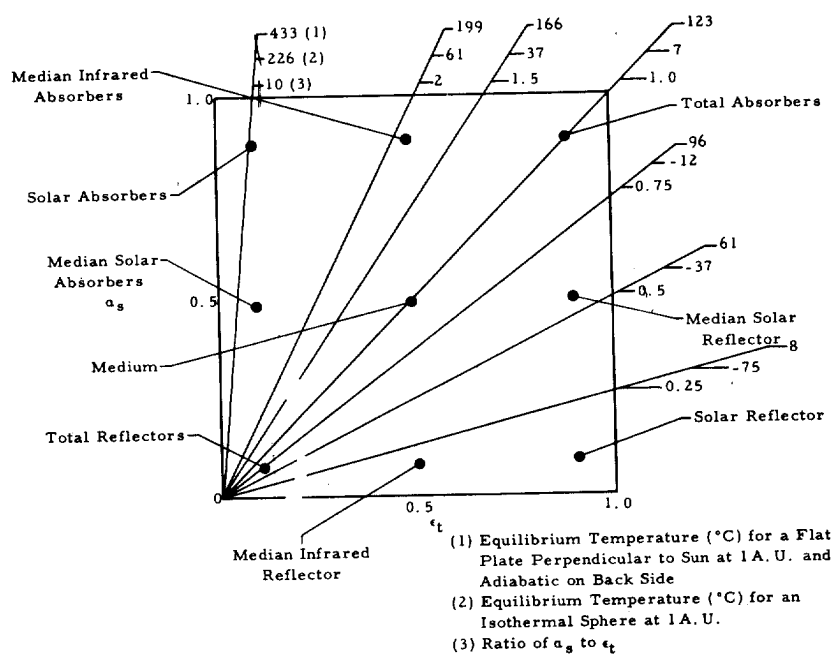
FIGURE 6.—Basic types of surfaces.

METHODS FOR OBTAINING SURFACES WITH DESIRED CHARACTERISTICS

For the purpose of discussion it has been found convenient to separate the means of obtaining various surfaces into the following categories:

1. Bare Metals
    a. Polished
    b. "As received"
    c. Sandblasted
2. Thin Films
    a. Vacuum-deposited (metallic and nonmetallic)
    b. Conversion
    c. Plated
3. Pigmented Coatings
    a. Paints (metallic and nonmetallic)
    b. Vitreous enamels
    c. Inorganic bonded
4. Transparent Coatings
    a. Conversion-coatings
    b. Nonpigmented paints
5. Paste-on Films
6. Special Coatings
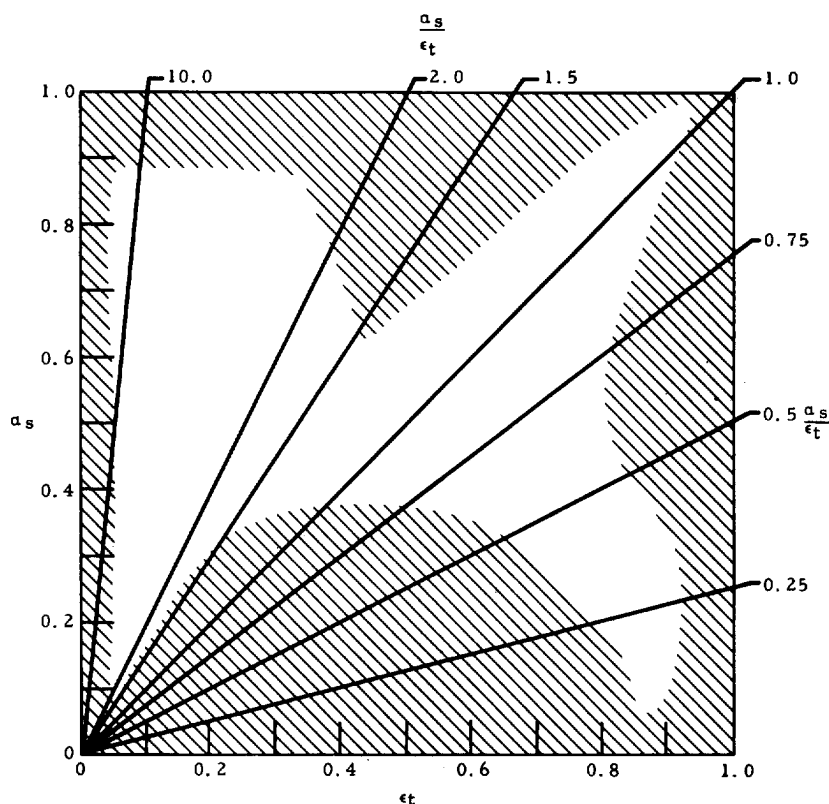
FIGURE 7.—Areas of overall progress.

The types of surfaces generally obtained from each of the above methods are shown in table 4.

In constructing the graphs for Utilization Requirements, ground rules were established and followed in determining which methods could be used to satisfy each of the utilization requirements. These rules are indicated in table 5 and are discussed in more detail along with a brief discussion of each type of surface and some of their individual characteristics. The desirability of surfaces with certain special optical properties is also discussed.

Bare Metals

The optical properties of bare metals are well known from theory and numerous measurements. Yet, when the designer is confronted with the use of this data he is at once at a loss to correlate this information with the exact surface condition of the metal he is considering.
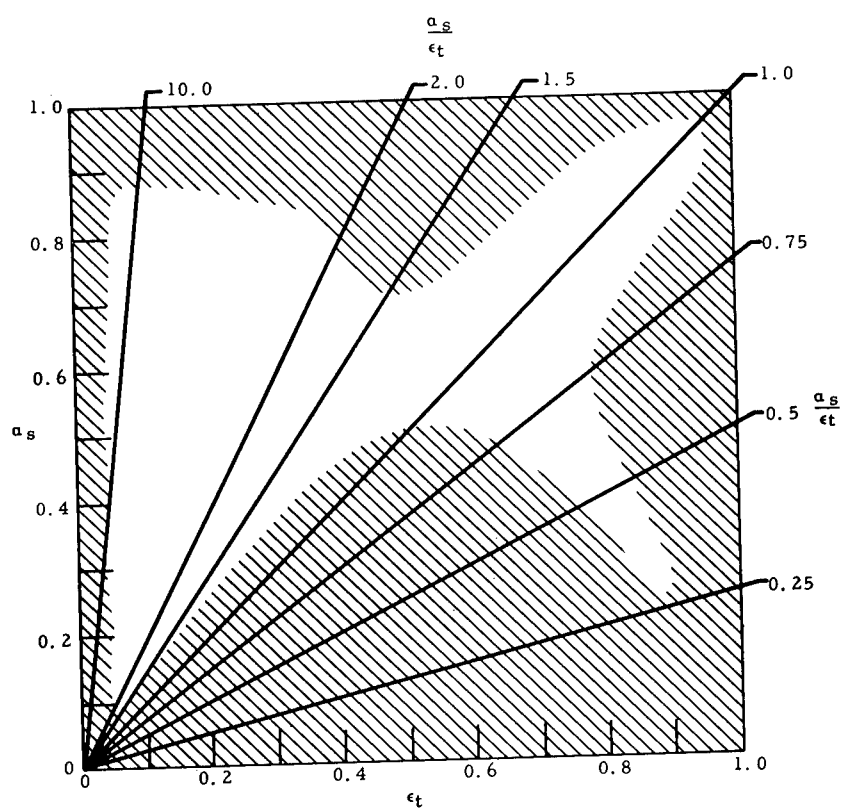
FIGURE 8.—Ultraviolet-stable surfaces.
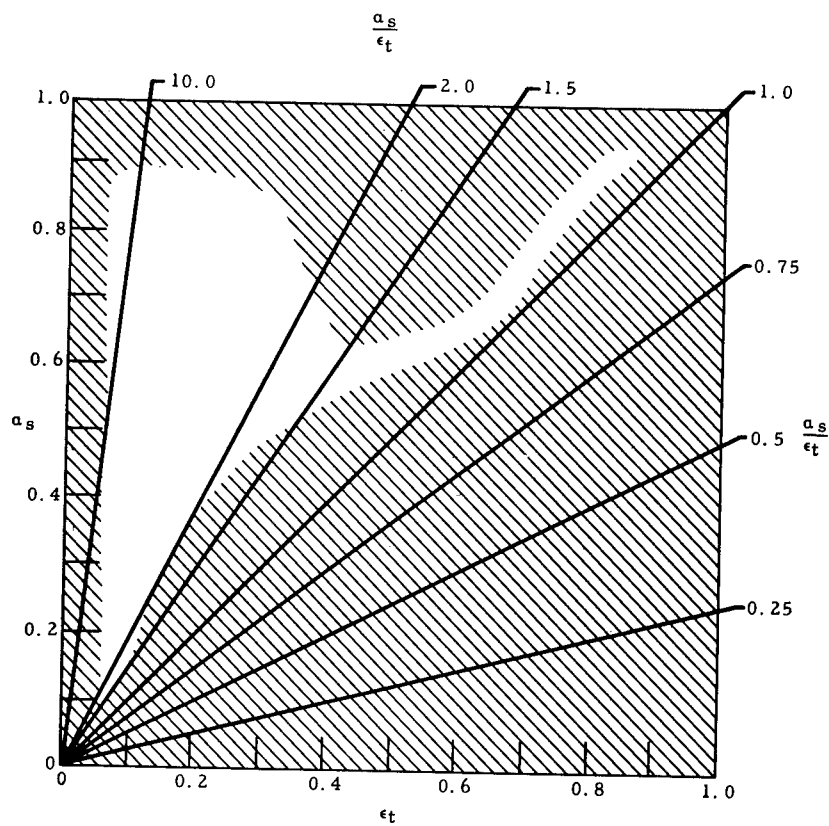
FIGURE 9.—"Thin" surfaces, electrically-conductive surfaces.
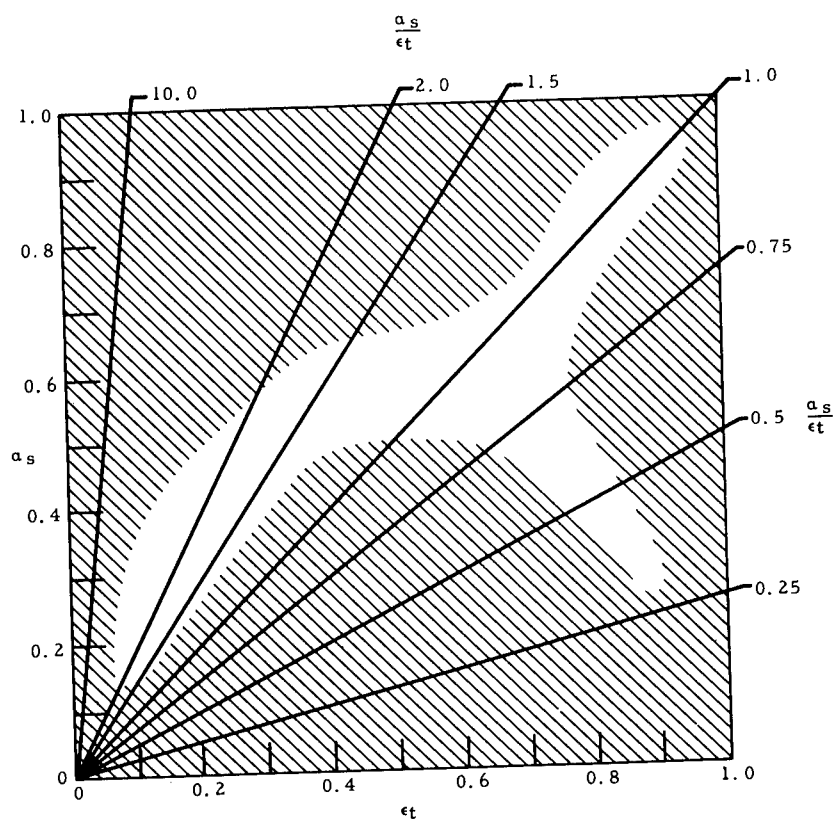
FIGURE 10.—Large area surfaces.
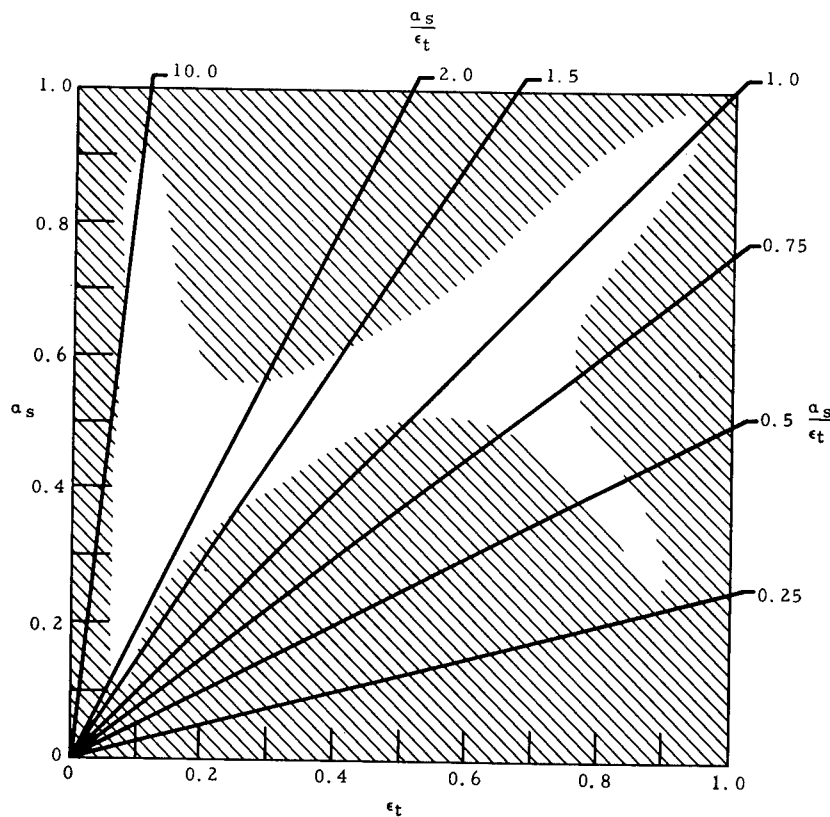
Figure 11.—Repairable or prelaunch stable, ascent-stable surfaces.

He must consider such fundamental optical properties as solar absorptance, (α), if it is to be exposed to solar irradiation, and total hemispherical emittance, (ϵ). Secondly, he will consider the spectral characteristics of his material, $(\epsilon\lambda)$, according to the nature of other radiations to which it is to be exposed (i.e., such as planetary radiation). Going back and considering the solar absorptance, (α), the designer must find the average of the solar absorptance at a particular aspect angle, $(\alpha\theta)$. Also, angular dependence of (ϵ) is important if various surfaces are exposed to each other.

For accuracy it is necessary to determine how precisely the optical properties are known for a particular surface. For most polished metals the emittance is low compared with the solar absorptance. Consequently, the ratio can be quite different depending on the uncertain accuracy in measurement. For example, aluminum can have an emittance of about

TABLE 5.—*Thermal Control Surfaces vs. Utilization Requirements*

	Ultraviolet stable	"Thin"	Electrically conductive	Large surfaces	Reparability and/or prelaunch stable	Ascent stable
Bare Metals						
(a) Polished	X	X	X	X	S	S
(b) "As Received"	X	X	X	X	S	S
(c) Sandblasted	X	X	X	X	S	S
Thin Films						
(a) Conversion	S	X	N	W/R	X	X
(b) Vacuum-Deposited						
(1) Metallic	X	X	X	N	N	S
(2) Nonmetallic	S	X	N	N	X	X
(c) Plated	X	X	X	W/R	S	S
Pigmented						
(a) Paints						
(1) Metallic	S	N	X	X	X	S
(2) Nonmetallic	S	N	N	X	X	S
(b) Vitreous-Enamel	S	N	N	N	X	X
(c) Inorganic-Bonded	S	N	N	W/R	N	X

KEY: X=yes; S=selective; W/R=with reservations; N=no.

0.03 and (α) of about 0.18 giving a (α/ϵ) of 6. If the uncertainties in the emittance measurements are +0.03 then the (α/ϵ) has a range of 3 to 6.

Metals have a wide range of surface conditions such as the "as received," oxidized, sandblasted, polished, and vacuum-deposited. (Vacuum-deposited is discussed later in this report.) In space applications, the latter three have received the most attention. The two primary methods for polishing are mechanical and chemical. Mechanical polishing "work hardens" the surface, and usually requires an abrasive which burnished into the surface creates additional uncertainties. Chemical polishing requires a bath and therefore needs to be performed prior to assembly. Sandblasting seems to give the most stable metal surface from the standpoint of handling since the (ϵ) value will be higher and small changes will not affect the (α/ϵ) ratio as significantly. Warpage of the metal as a result of sandblasting is a major problem.

In general, metals are considered space stable even for long periods of time. However, the vapor pressure and sputtering rates of some metals preclude their use in long-term applications.

Thus, since much of the exterior surface of most spacecraft is metallic to begin with, the optical properties which can be obtained from the bare surface are sometimes the ones desired. The use of bare metal surfaces

for thermal control is preferred to coated surfaces because bare metal surfaces generally are space-stable, have less weight, and require less time and money for their preparation.

Thin Films

Vacuum-deposited.—The vacuum-deposited coatings (both metals and dielectrics) presently represent one of the more expensive methods for obtaining surfaces with specific optical properties. However, a wide range of distinct values of (α) and (ϵ) can be obtained with very close tolerance, and the added weight is negligible.

Much of the expense is due to the necessity for large vacuum chambers and other coating facilities necessary to coat large rigid areas. Handling · is also a major problem as is corrosion protection (prelaunch environment) and the repairing of defects or handling scars. Vacuum-deposited metals are particularly subject to these hazards while the dielectrics are much more wear and weather resistant (ref. 6) and, to a certain extent, are cleanable.

Conversion coatings.—Almost all metal surfaces form a very thin, homogeneous, dielectric film. Usually, this film is an oxide of the parent metal and may even be monomolecular in thickness. Conversion coatings, in general, extend the thickness of this film by chemical conversion. The sparse data on such thin coatings show them to exhibit strong absorption in the infrared while retaining varying transparency in the visible region. Application requires a chemical bath, precleaning and rinsing baths, and exacting processing control for reliable and repeatable coatings.

There is little information available on the space stability of these coatings. Other considerations such as cost, weight, and handling made these generally-rugged coatings attractive for space applications.

Plated.—Plated coatings are limited to metals (electrically-conductive) but techniques have been developed making it possible to plate these coatings on various dielectrics.

As a rule, these coatings cannot be made as highly reflecting in the visible and infrared as are coatings prepared by vacuum evaporation, but adhesion is usually very good.

Pigmented Coatings

Paints.—Because of the obvious application and other advantages and the vast experience behind pigmented paints, much effort has gone into developing and testing this type of coatings for thermal control purposes on space vehicles. The results of these tests, especially ultraviolet degradation in a vacuum environment, proved that paints were not as stable as once thought. However, research and development have since produced pigments and vehicles that are relatively stable to ultraviolet-in-vacuum and fairly severe ascent-environments (refs. 7 and 8).

A large range of solar absorptance can be obtained because of the availability of many pigments (even low emittance can be obtained by using metallic pigments). However, almost all paints have an (α/ϵ) ratio of 1.0 or less; thus, the development of paints having higher ratios would be extremely desirable.

Vitreous enamels.—Very little work has been done with vitreous enamel coatings, probably because of the high temperatures ($\sim$800 to 1,250° K) required to fire the coating. It should be possible to obtain about the same range of optical properties with these coatings as with paints. High temperature operation, hardness, durability, and cleanability are the major advantages. Disadvantages are also numerous: a thick coating is required for good solar reflectance ($\sim$5 to 10 mils); the firing temperature is high; the coating is brittle; the coefficients of expansion must be carefully matched; the surface must usually be acid-etched or sandblasted prior to coating; and the coating is nonreparable.

Inorganic-bonded coatings.—Inorganic cements such as aluminum phosphate, potassium silicate, and sodium silicate, can be pigmented like a paint and applied to a surface. The results are very porous coatings which, as a rule, are oven cured at moderate temperature ($\sim$420° K). These coatings can be made very white (low α) and to have a high emittance and, hence, a low (α/ϵ) ratio. As in paints, a large number of pigments are available to give a wide range of (α) values. Resistance to degradation by ultraviolet has been reported (ref. 8) for some combinations of binders and pigments.

Flame and plasma-spray techniques offer excellent possibilities for applying inorganic materials to almost any substrate. These types of coatings were used on some of the first satellites (refs. 1 and 9) and undoubtedly will be used for thermal control coatings in many future cases. Although very low (α/ϵ) coatings have not been obtained, the range of optical properties of flame or plasma-sprayed coatings exceed that of paints.

The outstanding disadvantage of these types of coatings is porosity which makes handling and cleaning difficult.

Transparent Coatings

Transparent coatings, as used here, are coatings which are transparent (nonscattering) over most of the solar-energy-spectral region (0.2 to 3.5μ) and opaque to longer wavelengths.

Even though transparent coatings are easily applied and repaired, and have good handling properties and are cleanable, almost no data on these coatings are available.

The value of (α) is largely determined by the metallic substrate. If a low α is desired with a structural skin of, for example, steel, then the

metal has to be buffed, electropolished, or even plated to obtain the desired (or the minimum obtainable) values.

Conversion coatings.—Some surface-conversion coatings fit into the transparent-coating category. The solar absorptance and thermal emittance values of these coatings increase with thickness so that good control of these properties can be maintained. The advantages and disadvantages of thin-film conversion coatings discussed previously apply here also.

Nonpigmented paints.—Surfaces that strongly reflect solar radiation but exhibit high thermal emittance can be obtained by applying a non-pigmented paint or transparent vehicle directly to a metallic surface. While the solar reflectance and the thermal emittance may not be as high as for some dielectric-particle pigmented paints, coatings with only moderately low α/ϵ are generally adequate.

Paste-on Films

Many of the adhesive-backed, paste-on films available on the commercial market are metallic or metallized plastic films. The list could be extended to include conversion coatings, paints, etc., already discussed in this report. Tapes comprising these paste-on films have poor environmental stability due to their adhesive component.

Special Coatings

Directional surfaces.—Frequently the designer has data only on the optical properties (α) and (ϵ) which have been calculated from reflectance data taken near normal to the surface. This data is often insufficient to accurately describe the heat balance of a space vehicle. The variation in (α) with incident angle, for example, has been known, in some cases when using data on representative surfaces, to produce significant deviation from the predicted temperature (ref. 10). The value (α) for most real surfaces deviates considerably from the values (α) for normal emittance or total hemispherical emittance. The value (α) for total hemispherical emittance is higher for smooth metal surfaces and lower for most dielectrics.

The directional absorption and emittance of surfaces suggest the possible use of these parameters for added thermal control. For example, the radiation exchange between surfaces might either be enhanced or attenuated, or orientation to the sun could be used to help regulate the temperature of a radiator. A mathematical analysis is discussed in reference 11 relative to the control of radiation exchange using asymmetrically-grooved surfaces.

Highly reflective, metallic platelets, such as leafing aluminum paint pigments or a razor blade surface, arranged as shown in figure 12, should give very distinct directional properties because the plates are large in comparison to this spacing. Filling the space with a dielectric, such as a
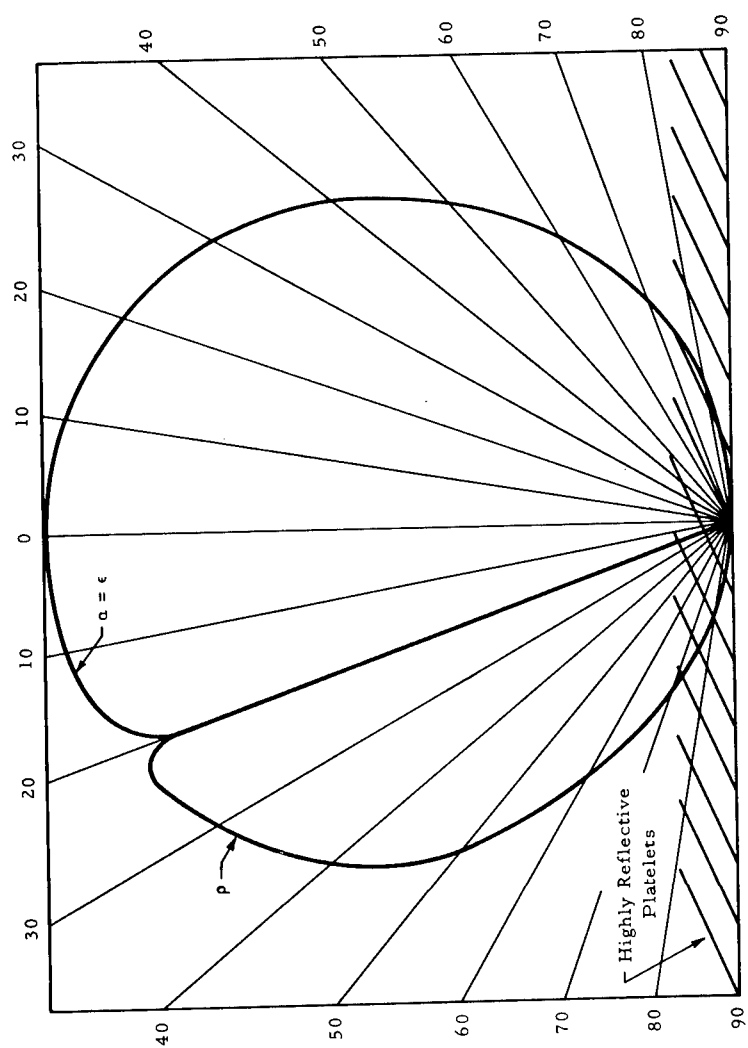
FIGURE 12.—Emission and reflection from highly reflective platelets 70° from normal (refractive index, $n = 1$).
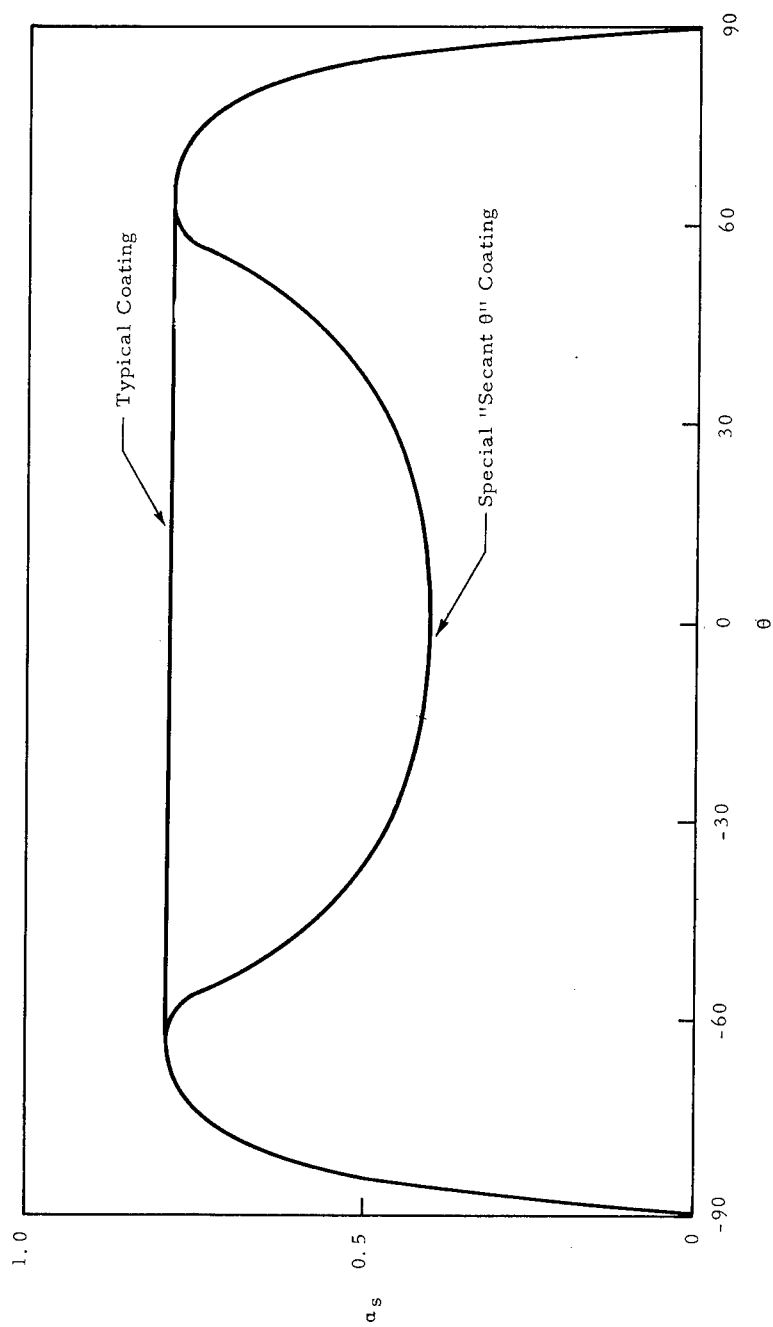
FIGURE 13.—Solar absorptance, α_s, versus aspect angle, θ.
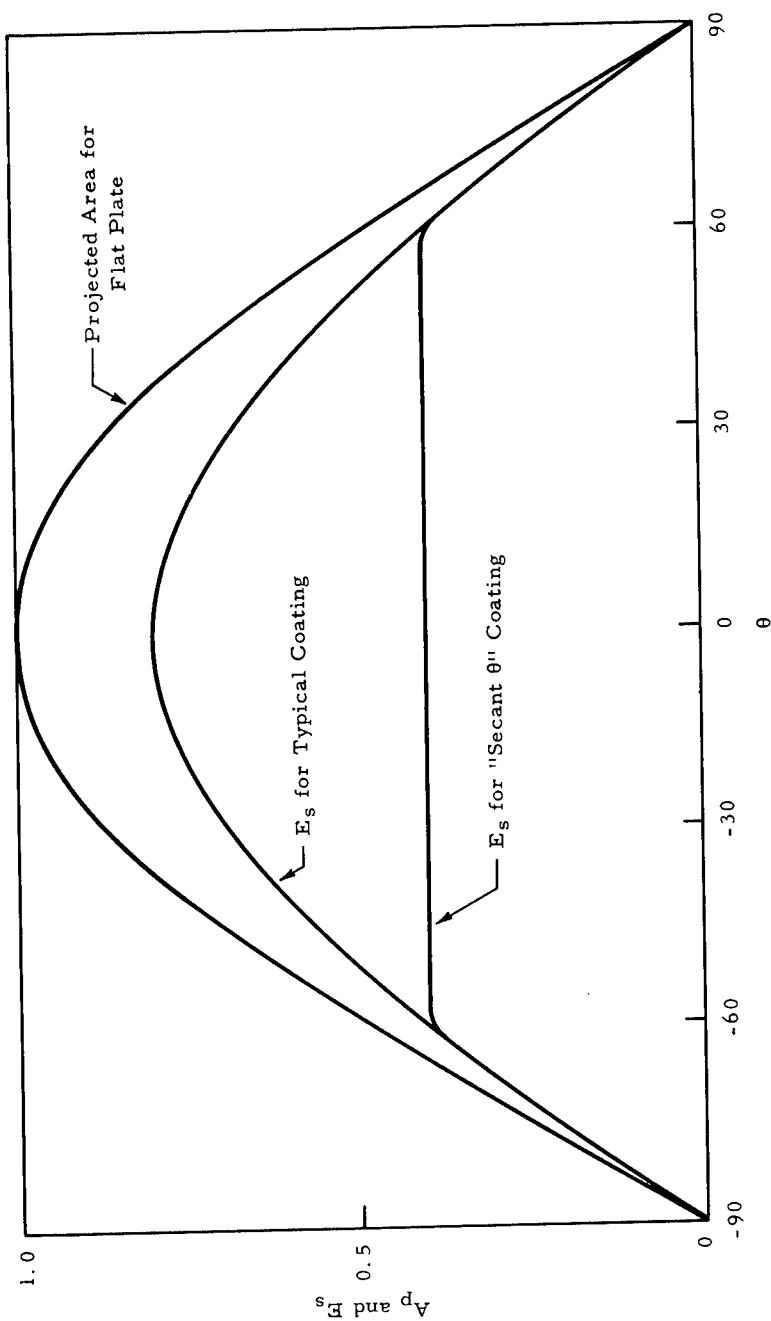
FIGURE 14.—Absorbed solar energy, E_s, and projected area, A_p, versus aspect angle.

paint vehicle, changes the directional characteristics. If the platelets are inclined at a low angle, the surface will have a lower (α) at near-normal angles than at the larger angles. If, with an arrangement such as this, a surface could be made whose (α) follows a secant function with respect to the aspect angle, then the variation in the amount of energy absorbed by a flat plate, due to the variation in projected area, would be largely cancelled, thereby giving a constant amount of absorbed energy (figs. 13 and 14).

Interference coatings.—Multilayer coatings can be applied to produce either constructive or destructive interference with the reflectance of a surface over some wavelength range. Very high (α/ϵ) (solar-absorbing) coatings have been produced on aluminum substrates using this technique. The same techniques can be employed to obtain very low (α/ϵ) coatings for solar-collectors and other applications.

Recent interest in infrared filters has greatly enlarged the overall technology of interference coatings to such an extent that their use as thermal control coatings should certainly be considered further.

Nonspectral.—A type of surface useful in many applications is a nonspectral or "gray" surface. The spectral absorptances of such surfaces are shown in figure 15. They would have a constant spectral absorptance throughout the solar region (assumed to extend from 0.1 to 3.0μ), and a perhaps different constant absorptance throughout the far infrared $(>3.0\mu)$. Such surfaces would be desirable for thermal control of spacecraft because, for example, when undergoing ground thermal testing, the spectral distribution of any solar simulators would not be as critical (within the range of 0.1 to 3.0μ) and, thus, only the intensity would have to be carefully controlled. This is especially important when the spectral distribution of various available "solar simulators" is considered.

It is known that the earth and atmosphere radiate infrared radiation to space with a total intensity about the same as that from a blackbody at 248° K. However, the spectral distribution (typically) is much different as shown in figure 16 (ref. 12). If a surface is nonspectral in the far infrared, the absorption by the surface of the earth and atmospheric radiation, (α_E), is the same as the absorption-to-radiation from a 248° K blackbody, $(\alpha_{248}$ °K$)$. In most satellite design work it is usually assumed that (α_E) is equal to (ϵ). Generally, this is a fairly safe assumption. However, figure 13 shows two hypothetical surfaces having (α_E) values very different from $(\epsilon_{248}$ °K$)$ (or α_{248} °K$)$. Even though the $(\epsilon_{248}$ °K$)$ values are 0.61 for both surfaces, the (α_E) values are 0.46 in one case and 0.71 in the other.

Because the spectral characteristics of thermal control surfaces may be

Far Infrared Region

$$\frac{a_s}{\epsilon_t} = \frac{0.2}{0.8} = 0.25$$

Medium Surface, $\frac{a_s}{\epsilon_t} = \frac{0.5}{0.5} = 1.0$

$$\frac{a_s}{\epsilon_t} = \frac{0.9}{0.4} = 2.25$$

Solar Region

λ (Microns)

a_λ

1.0

0.5

0.1   1.0   10.0   100.0
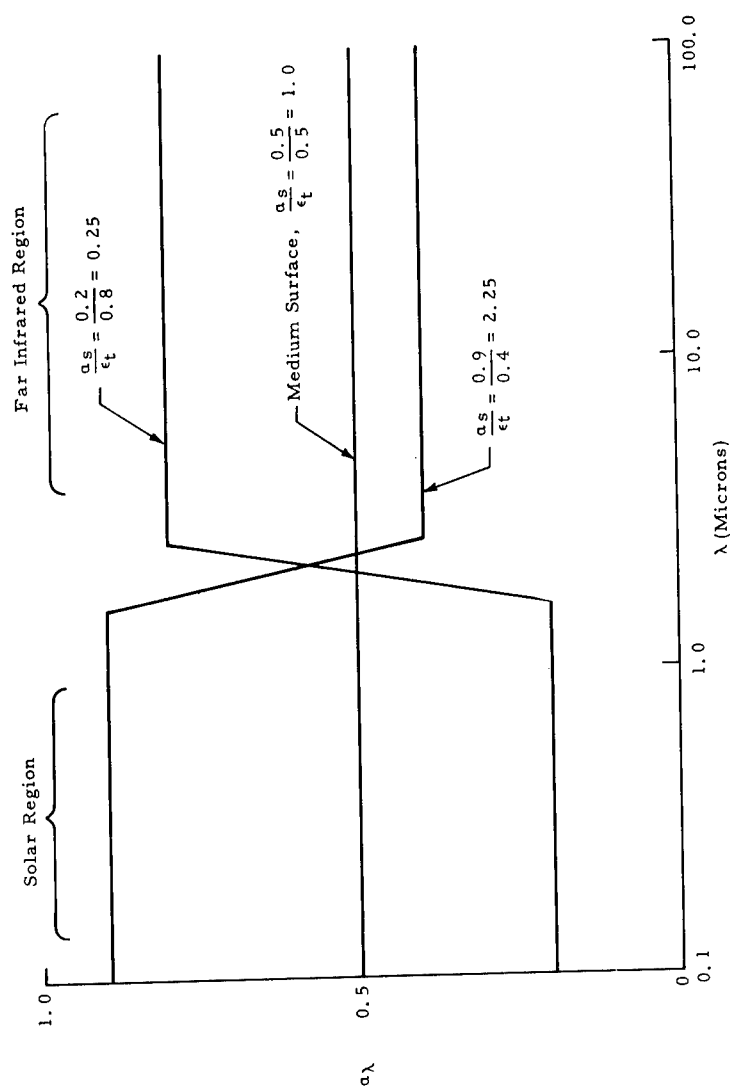
Figure 15.—Examples of some ideal nonspectral surfaces.
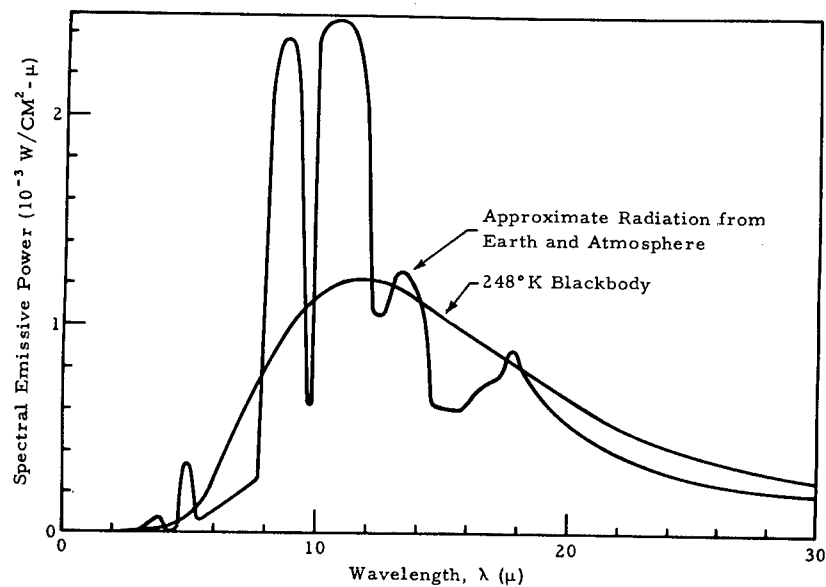
FIGURE 16.—Spectral energy distribution of earth and atmosphere compared to 248° K blackbody.

strong tools in spacecraft thermal design work, additional investigation in this area might be extremely fruitful.

Controlled degradation.—It should be mentioned briefly that the degradation of a surface in space might not always be undesirable. One example would be on a one-way trip to Mars in which the increase in the distance from the sun could cause the temperature of the spacecraft to drop. If the coating degraded from solar irradiation in a manner as shown in figure 13, the increase in distance would be balanced by an increase in solar absorptance and, thus, maintain a constant on-board temperature. It should be noted that figure 13 is based on "equivalent earth sun-hours exposure," a unit used to present ultraviolet-degradation data. Thus, even though the time required for the trip is about 6,000 hours, the "equivalent exposure" time is about 3,900 hours.

Before controlled degradation coatings can be fully utilized, more theoretical and experimental work is needed to clarify the mechanism and environment-factors responsible for degradation.

Self-regulating or inflight-variable surfaces.—Surfaces which have optical properties that can be varied in flight by either passive or active means are desirable. Research in this area has apparently yielded very little useable results thus far. Further discussion of the efforts in this area is beyond the scope of this paper.

CONCLUSIONS

At first glance, with the exception of the median-infrared reflectors and absorbers, there appears to be a large selection of coatings and surfaces with a wide range of optical properties (α, ϵ, and α/ϵ). However, definite gaps appear when the following representative utilization requirements are imposed:

1. Ultraviolet stable
2. Thin coatings
3. Electrically conductive
4. Applicable to large areas
5. Reparable or prelaunch stable
6. Ascent stable

These gaps widen severely when two or more constraints are considered.

To alleviate the loss in the choice of optical properties available to the designer due to particular utilization requirements, there is need to further develop coating technology, both in optical properties and application techniques.

Also, in extending passive coating technology for thermal testing and design, it would be desirable to develop such special surfaces as:

1. Directional surfaces
2. Interference coatings
3. Nonspectral coatings
4. Controlled-degradation coatings

It is obvious that the development of thermal control surfaces is only in its infancy. Much work must be done before it will be possible to safely assume that individual "crash" programs will not be necessary to satisfy the thermal-design needs for most of the future spacecrafts.

In addition to this summary section it is necessary to stress the importance of developing active-temperature-control surfaces of the thermophototropic type being developed in the Thermal Control Group at Goddard Space Flight Center and other active systems being developed by Dr. O'Sullivan at Langley Research Center. These coatings must meet foreseeable future needs in the most efficient manner.

Details of several examples of temperature control coatings, which have been developed and are subject to further improvement, are discussed later in this report.

Although energy conversion coatings form a second group of coatings for space vehicle application because of their importance, they have received less attention than temperature control coatings. There are basically two types of solar energy conversion coatings to consider: (1) Carnot heat engine systems, and (2) direct electrical production coatings. Both types will be required for different applications over the next decade, but the direct electrical output coatings will be of greatest utility.

Three different types of coatings are required to operate a Carnot engine: (1) concentrator surfaces; (2) collector surfaces; and (3) dissipator surfaces for rejecting heat. The optical surfaces required for each of these three types of coatings are different. Concentrator surfaces must possess high solar reflectivity, with specular reflectivity being particularly desirable for purposes of optical focusing efficiency. Collector surfaces must possess maximum solar absorptance and minimum emittance. While dissipator surfaces require high hemispherical emittances, their solar absorptance is a minor consideration. Because a pointing system is required to point the concentrator toward the sun, the dissipator can be designed to point in the opposite direction. The optimum design would use the back surface of the collector structure as the dissipator.

Direct electrical production in space is currently limited to silicon semiconductor devices of the PN type. The Russian solar cells appear to be of the NP type which offer advantages in the presence of proton fluxes. The photovoltaic type cells are also potentially useful for direct electrical production, and current NASA research in this direction is discussed under Energy Conversion Coatings.

TEMPERATURE CONTROL COATINGS

FLAME-SPRAYED COATINGS

The first United States space vehicle, Explorer 1, achieved orbit at 3 hr 55 min 5 sec Greenwich mean time on February 1, 1958. The average orbit altitude was 900 miles with an inclination of 33.34° to the earth's equator. Explorer 1 was cylindrical shaped, 80 inches long and about 6 inches in diameter (fig. 17). The instrumentation section, consisting of a 20-inch length, capped with a 12-inch cone, was the only part with a temperature control coating. The remainder of the vehicle's surface was not coated.

Thostesen, Hibbs, and Buwalda (ref. 3) reported on the design parameters, the coating design, and the performance of this temperature control system. The thermal control system was exposed to aerodynamic heat during launch, thereby imposing a design restraint upon the coating which is seldom encountered now because most space vehicles are shrouded. The outer shell was made using stainless steel of two different types; the cone had an (α/ϵ) ratio of 4.12, and the cylindrical shell had a value of 1.92. Because these values of (α/ϵ) would produce excessively warm temperatures, a predetermined striped low (α/ϵ) coating of Al_2O_3 having an (α/ϵ) value of 0.437 was applied.

The Norton Company's "Rokide A" coating, (98 percent Al_2O_3) was applied to the cylinder at the Jet Propulsion Laboratory using Norton's patented process. The areas to be coated were sand blasted with white sand; subsequently, the Rokide coating was applied and the edges of the

1 Fiberglas Rings
2 Launching Surfaces
3 Micrometeorite Erosion Gages (12 Each)
4 Internal-Temperature Gage
5 Turnstile Antenna Wire
     (4 Each, 22 1/2" Long)
6 External-Temperature Gage No. 1

7 High-Power Transmitter
8 External Shell
9 Internal Shell
10 Micrometeorite Impact Microphone
11 Cosmic-Ray and Micrometeorite
     Package
12 External-Temperature Gage No. 2
13 Low-Power Transmitter
14 Nose Cone (Stainless Steel)
15 Nose-Cone Temperature Probe

FIGURE 17.—The 1958-α satellite.

coating trimmed to the required geometry with a carboloy tipped scribe. By a similar process, a coat of "Rokide A" was also applied to the cone at the Marshall Space Flight Center.

Temperatures were measured at four points: (1) stagnation temperature of the cone tip; (2) nose cone skin temperature; (3) cylinder skin temperature; and, (4) internal temperature. The accuracy of the first two measurements was approximately ±20° C, ±3° C for No. 3 over the range −10° to +80° C, and ±2° C from 0° to 30° C up to ±20° C at 90° C for measurement No. 4. Since no prior data was available, obtaining temperature information was the prime purpose for launching the Explorer vehicle.

Predicted and actual temperatures during the flight are shown in figure 18. While the flight data tended to indicate a lower temperature than the design temperature, the agreement was quite satisfactory considering the limited experience then available.

VACUUM COATINGS

The thermal and optical design of Vanguard II reported by Hass, Drummeter, and Schach (ref. 2) represented the most sophisticated
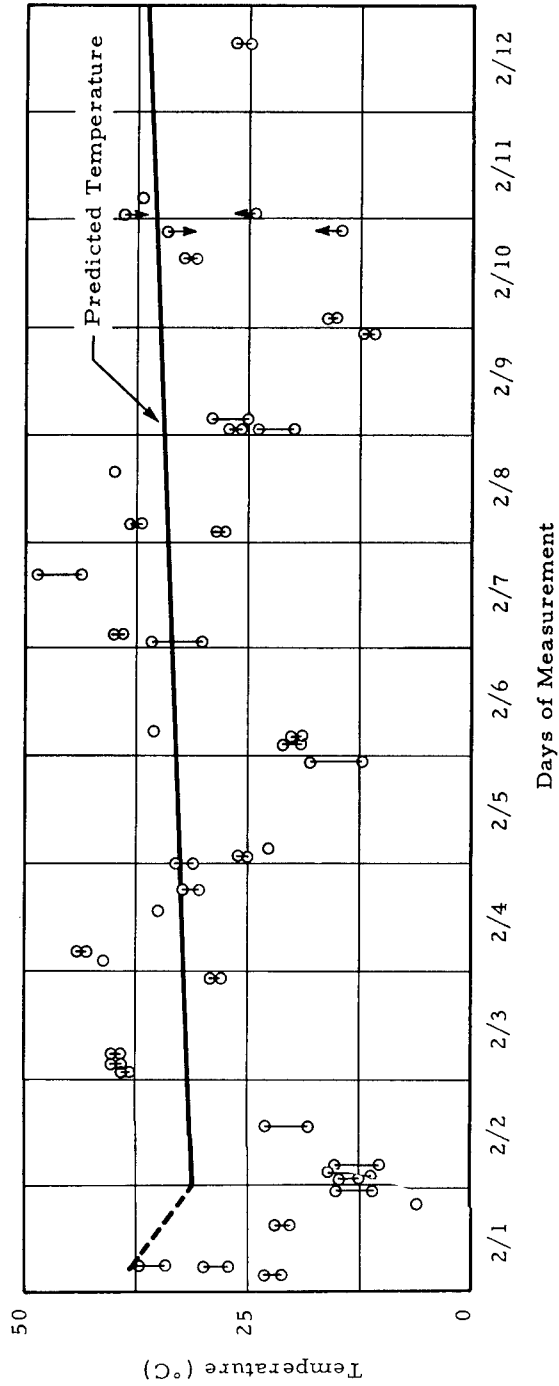
FIGURE 18.—Measured and predicted internal-cone temperature versus time for 1958-α satellite, 1 through 12 February 1958.

coating developed for any known space vehicle in early 1959. Because Vanguard II (a 20-inch diameter spherical shell) was to be used in visual satellite tracking experiments, it was provided with a highly-reflecting specular surface to assure maximum visibility. Due to payload electronics requirements, the desirable temperature range was 10° to 60° C with approximately 26° ± 3° to 31 ± 3° C as the optimum range. Because the requirements of a highly-reflecting surface, i.e., low solar absorptivity and specific (α/ϵ) ratio, are not independent variables, the desired (α/ϵ) of 1.3 had to be achieved with as low values for both quantities as was possible.

The final coating developed to meet these requirements (fig. 19) was a multilayer, vacuum-deposited coating. The basic satellite shell was magnesium alloy, which was gold plated. A 500Å layer of chromium was deposited on the gold surface as a primer to promote adherence. The second layer was a 500Å layer of silicon monoxide that served as a diffusion barrier between the third layer—a 1,000Å coating of aluminum—and the chromium layer. The aluminum layer provided the high reflectivity required for maximum visibility. The fourth layer was a 6,000Å layer of silicon monoxide for temperature control purposes.

The change in emissivity of aluminum coated with three different thickness layers (5,400Å, 7,200Å, and 12,000Å) of silicon monoxide is shown in figure 20. This coating used the strong resonance absorption band by silicon monoxide at 10μ to greatly increase the emissivity, while altering the reflectivity only a few percent. In addition, the absorption band was so located with respect to the blackbody radiation curve of the satellite, that increases in the satellite temperature caused a larger proportion of energy to fall within the absorbing region. Therefore, as the emissivity increased with temperature, and the (α/ϵ) value was decreased, a degree of self-adjusting temperature correction was offered. Furthermore, an additional advantage was gained from the broadening of the absorption band with increasing temperature.

The vacuum coatings were applied in a 72-inch evaporator operated at a total pressure of 8 to 10 × 10^{-5} Torr. The satellite was held in a specially designed yoke which rotated the sphere in such a manner as to deposit a uniform coating on all surfaces. The substrate was cleaned using a 6,000 v dc glow discharge at 400 ma for about 15 minutes. The electrical discharge heated the sphere to 150° C, thereby completely outgassing the outer surface with assurance of a better adherence of the coated layers. Coatings were deposited at the approximate rate of 100Å/min. The view factor from the evaporator source to the satellite was restricted to an angle of incidence of less than 45° in order to prevent the formation of rough surfaces inherent in greater incidence angles. Coating thicknesses were measured during deposition by an optical system.

SiO   t=6000A

Al   t=1000A

SiO   t=500A

Cr   t=500A

Gold-plated Magnesium
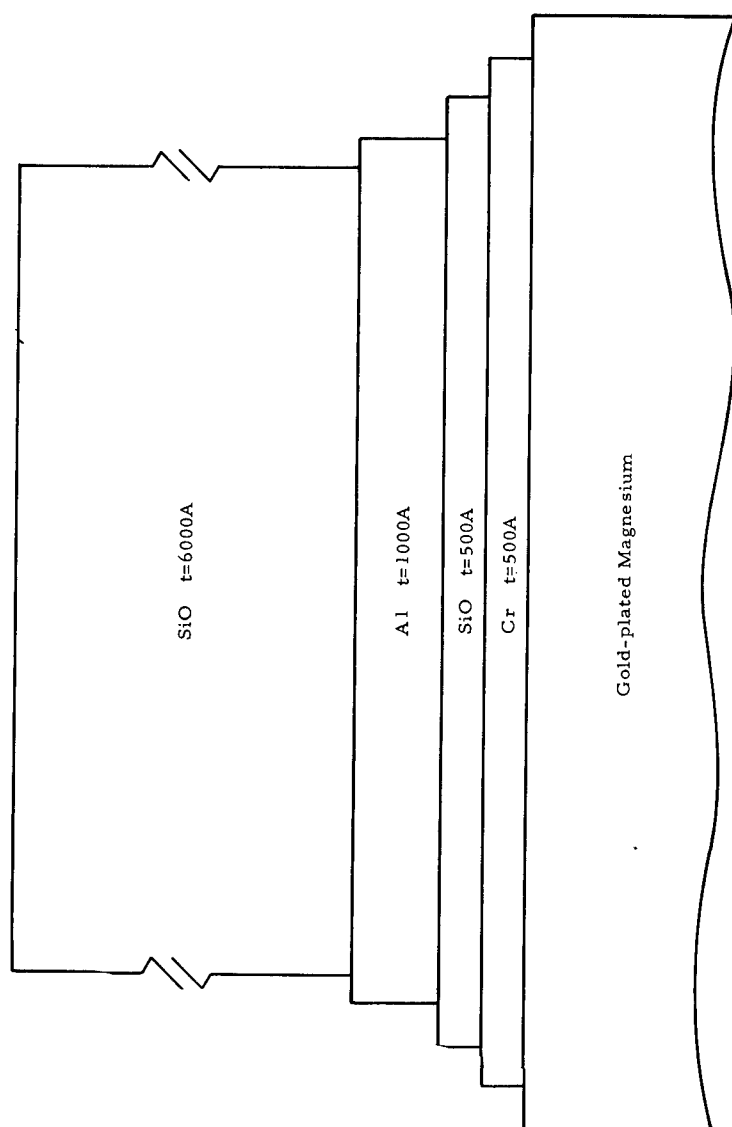
FIGURE 19.—Durable multilayer coating developed for Vanguard 20-inch shells to provide optimum-visibility and temperature-stability.
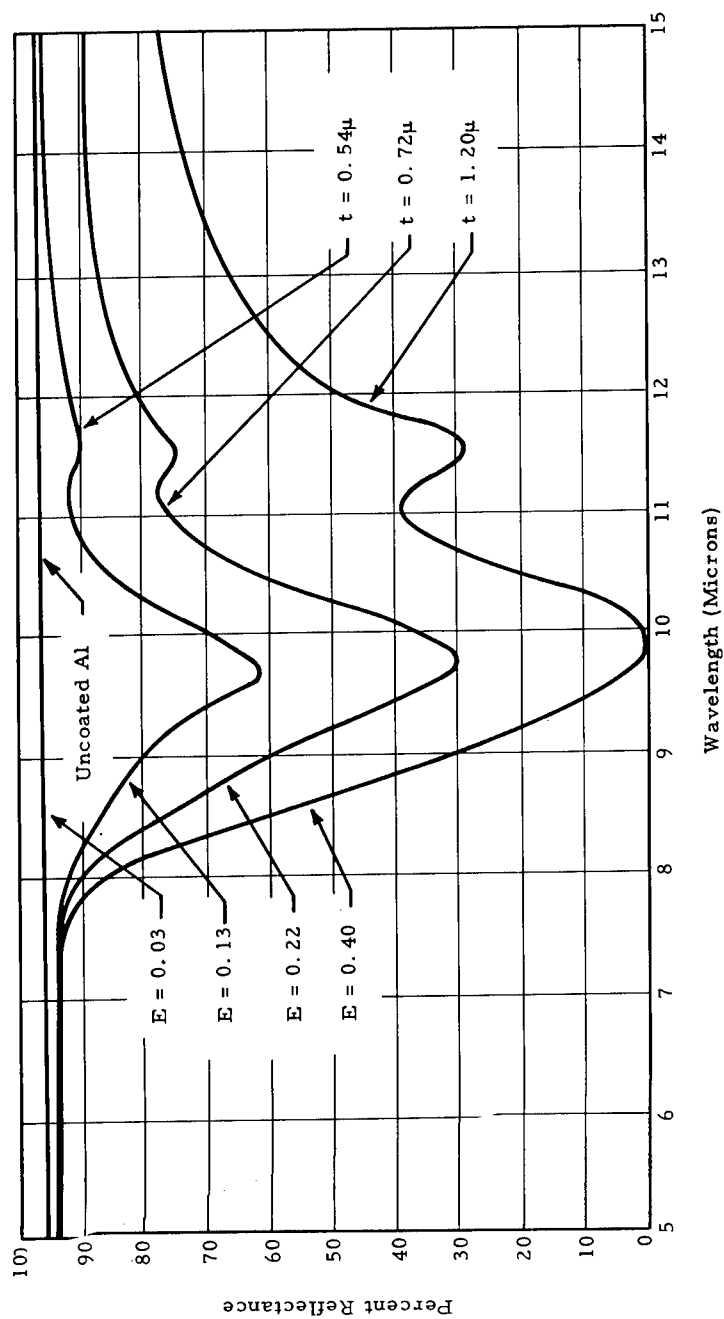
FIGURE 20.—Infrared reflectance and heat emissivity (at 20° C) of aluminum with and without silicon monoxide coatings of various thicknesses.

Vanguard II was placed in orbit on February 17, 1959 with a perigee of 350 miles, an apogee of 2,065 miles directed away from the sun, a 33.4° orbit inclination and a solar declination of 11° south. The percent time of direct solar exposure was 69 percent. Assuming an earth blackbody temperature of 255° K, and an albedo of 30 to 50 percent, a mean orbital shell temperature of between 20 and 25° C is calculated for an inert satellite, and between 26° ± 3° C and 31° ± 3° C depending upon the earth's albedo. The satellite in orbit achieved an equilibrium temperature of 34° C one week after launching and performed satisfactorily.

The vacuum coating of objects is still, in a good measure, art as well as science. The performance of Vanguard is a tribute to the careful techniques and experience of Dr. Hass of the U.S. Army Engineer Research and Development Laboratories, Fort Belvoir, Virginia. Unfortunately, it is not yet possible to transmit complete details of vacuum coating techniques. This satellite had the most sophisticated inorganic coating system designed and produced for temperature control purposes to February 1959.

ALUMINUM-CONVERSION COATINGS

Dr. William J. O'Sullivan, Jr. conceived a number of space vehicles based upon inflated structural concepts. Echo I and Echo II were used as passive satellites, and Explorer IX was designed to measure the density of space environment near the earth. Restrictions on payload weight and cost limitations clearly indicate that thermal control systems must be lightweight, cheap, and applicable to large areas. General details of these structures were given by Pezdirtz (ref. 13).

The Echo I satellite (fig. 21) was constructed of 0.5 mil-thick mylar film coated with an opaque external layer of vapor-deposited aluminum. The satellite was a sphere 100 ft in diameter and inflated with 10 lbs benzoic acid and 20 lbs anthraquinone. Such a structure is quite large, having a volume of just over ½ million cu ft and a surface area of about 33,000 sq ft. Thermal control was provided by the vapor-deposited aluminum, which was applied primarily to reflect electromagnetic energy. The operating temperature was calculated to be 115° C, sufficient to keep the pressurizing materials in the gaseous state.

Echo II followed Echo I to further demonstrate the long-term usefulness of inflatable space structures. This satellite (fig. 22) was constructed (ref. 13) of a 3-layer laminate; a 0.18-mil thick layer of 1,080 aluminum on each side of a 0.35-mil thick mylar film. The 135-foot sphere had an approximate volume of 1¼ million cu ft and a surface area of 57,300 sq ft (~1.3 acres) and weighed about 500 lbs. Inflation was achieved by the vaporization of 38 lbs of pyrazole.

Thermal control coatings developed for Echo II were described by Clemmons and Camp (ref. 14). After a survey of the coating field it was
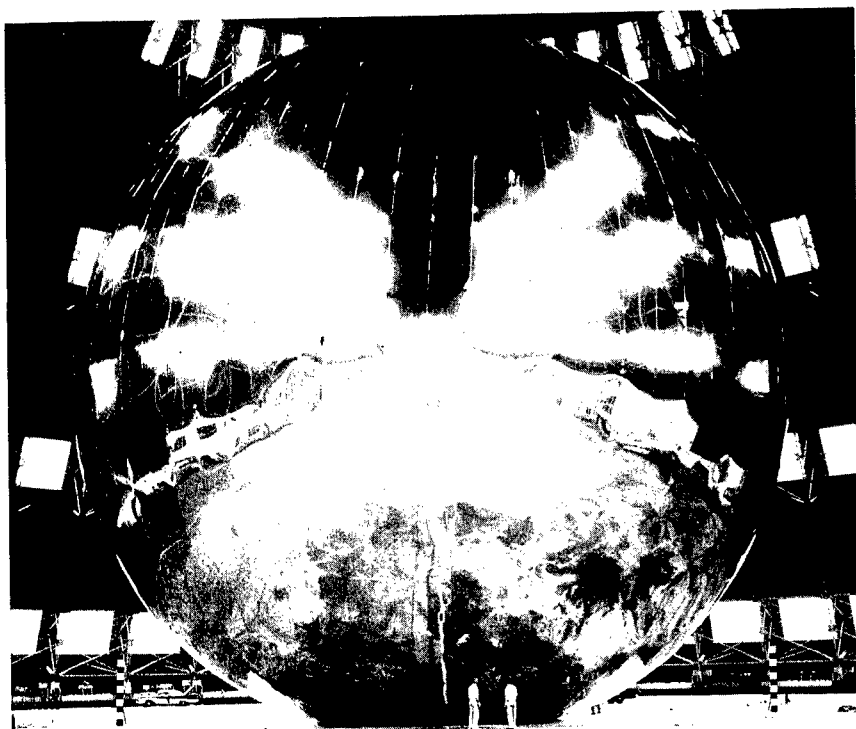
FIGURE 21.—NASA Echo I, 100-foot diameter inflatable spherical passive communications satellite.

found that the "Alodine 401–41" and "Alodine 1200S" produced using proprietary solutions of the Amchem Products, Inc., Ambler, Pennsylvania, appeared most promising. These coatings were amorphous, phosphate coatings on aluminum, originally developed as protective surfaces and paint primers for aluminum-coated, steel-wire fencing. The aluminum foil laminate as prepared had an emittance of 0.03 and a solar absorptance of 0.18 giving a (α/ϵ) value of 6.0, indicative of an orbital temperature of 181° to 210° C, which would impair the strength of the laminate.

An aluminum surface is treated by painting, dipping, or spraying with the "Alodine" solutions, which consist of a mixture of chromic ,phosphoric and hydrofluoric acids of varying proportions. The (α/ϵ) values of aluminum laminate surfaces, after immersion for various lengths of time in "Alodine 401–41 and 1200S," are shown in table 6. The (α/ϵ) range of 7.5 to 0.82 was obtained with a weight increase of from 30.4 to 426 mg/ft². The desired (α/ϵ) ratio was achieved with a weight gain of about 200 mg/ft².
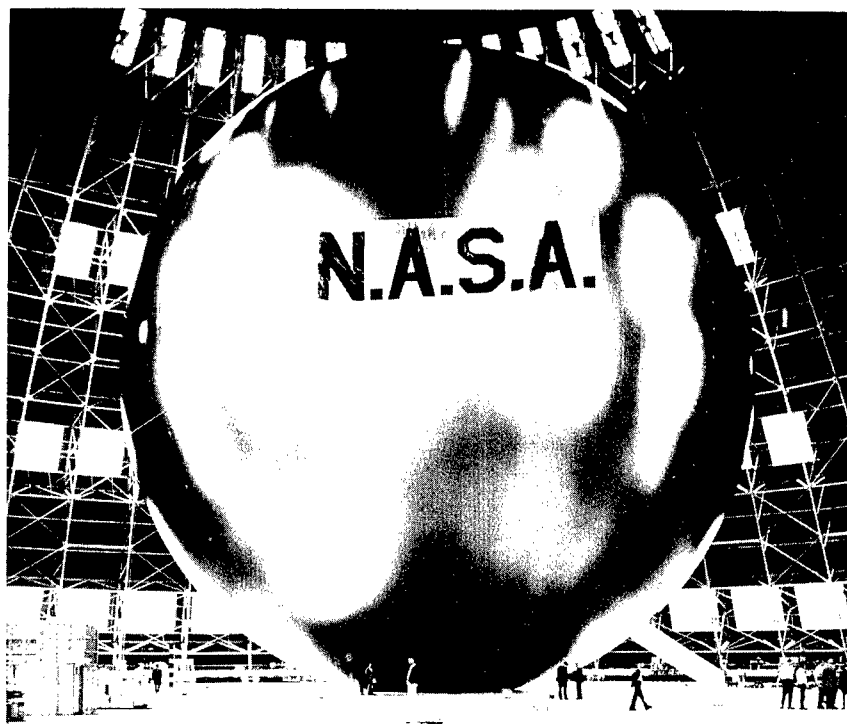
FIGURE 22.—NASA Echo II, 135-foot rigidized inflatable spherical passive communications satellite.

The "Alodine" treatment was very practical because the laminate was produced in 54-inch wide strips; the laminate could be pulled through the bath at a controlled rate to produce the coating thickness required. Laminate surfaces were first cleaned in an inhibited mild alkaline solution having the commercial designation "Ridoline 105." After the "Alodine" treatment, the laminate was rinsed with water and dried.

Chemical and spectrographic analysis of typical coatings indicate 18 to 20 percent Cr, 4 to 5 percent Al, 15 to 17 percent P, and 0.2 percent F. The main constituents are assumed to be 50 to 55 percent $CrPO_4$, 17 to 23 percent $AlPO_4$ and 22 to 33 percent water. In general, the coatings are insoluble in water, alcohol, solvents, most dilute acids, and alkalis. They are soluble in molten sodium nitrate and slightly soluble in concentrated nitric acid. The water can be driven off by heating.

Pezdirtz and Wakelyn (ref. 15) have developed an alkali-modified, phosphate-conversion coating, and investigated the ultraviolet and vacuum stability of the "Alodine 401–45" and the modified coating. They examined the infrared absorptance spectrum obtained for "Alodine 401–45" and determined that the peak, in the region of 3.8 microns, was

due to acidic hydroxyl groups; and the broad absorption band, between 7.5 and 11μ, was due to phosphate groups.

Since a 300° K blackbody has less than 1 percent of its total energy in the wavelengths shorter than 4.0μ and 25 percent between 7.5 and 11μ, the hydroxyl group vibrations near 3.8μ make an insignificant contribution to the emittance of the coating. If the hindering effect of hydrogen bonding on the molecular vibrations of the P–O bonds could be reduced by removal of acidic hydrogen through treatment with a base, the emittance obtained per unit weight could be substantially increased. Alteration of the phosphate groups can be obtained by varying the reaction as follows:

$$
\begin{array}{c}
O \\
\uparrow \\
HO-P-OH \\
| \\
OH
\end{array}
\;
\underset{+H^+}{\overset{-H^+}{\rightleftharpoons}}
\;
\left[
\begin{array}{c}
O \\
\uparrow \\
HO-P-O \\
| \\
OH
\end{array}
\right]^{-1}
\underset{+H^+}{\overset{-H^+}{\rightleftharpoons}}
\left[
\begin{array}{c}
O \\
\uparrow \\
HO-P-O \\
| \\
O
\end{array}
\right]^{-2}
\underset{+H^+}{\overset{-H^+}{\rightleftharpoons}}
\left[
\begin{array}{c}
O \\
\uparrow \\
O-P-O \\
| \\
O
\end{array}
\right]^{-3}
$$

<div align="center">
Orthophosphate　　Orthophosphate　Metaphosphate
(di-H)　　　　　　(mono-H)
</div>
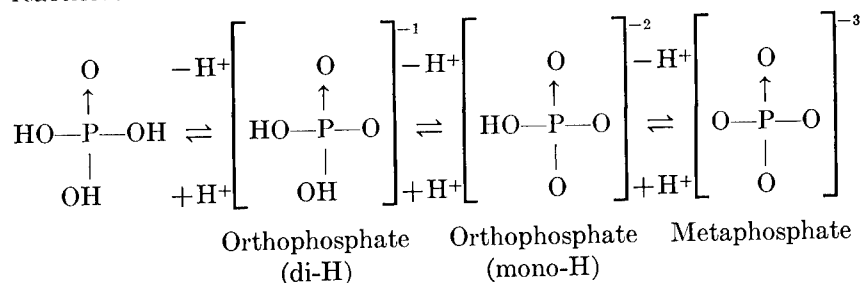
A series of experiments was carried out to test this hypothesis by treating "Alodine 401–45" coatings in dilute sodium and potassium hydroxide solutions for periods of 10 to 60 sec. The emittance of the treated coating increased linearly with time, changing from 0.2 to 0.4 in 60 sec. The absorptance changes only slightly, resulting in a net change in (α/ϵ) from 1.1 in the untreated surface to a value of 0.5 after 65 sec of hydroxide treatment. Thus, lower values of (α/ϵ) can be obtained for a given coating thickness or the weight of a coating can be reduced by about 50 percent. This is an important improvement in coatings for satellite-thermal-control purposes.

Pezdirtz and Wakelyn (ref. 15) also investigated the stability of phosphate coatings by subjecting samples to the equivalent of 3 to 4 suns intensity emitted by a BH-6 lamp. Temperatures of 0° and 70° C and a 10^{-6} Torr pressure were used as well as 1 Torr at 100° C and 10^{-7} Torr at 25° C. This selection of temperatures and pressures was made to separate temperature-effects from ultraviolet-degradation. After exposure in vacuum, samples were brought out into the atmosphere for measurement of (α) and (ϵ).

In general, the 100° C thermal test and the 25° C ultraviolet tests increased the value of (α) by 10 to 20 percent and decreased the emittance, giving rise to an undesirable increase in (α/ϵ). The sample held at 0° C exhibited the converse effect; namely, an increase in (ϵ), a decrease in (α), and a decrease in (α/ϵ). It was assumed that the water was trapped in

TABLE 6.—*Alodine Thermal Characteristics*

Alodine	Immersion time (sec)	Surface density mg/ft^2	Temperature °C	ϵ	α_S	$\alpha_{S/\epsilon}$
401–41	15	30.4	−2 48 94	0.0410 .0465 .0460	0.331	7.12
,,	30	40.0	2.7 57 97	.0520 .059 .059	.357	6.05
,,	60	83.2	0 44 96	.071 .082 .087	.343	4.18
,,	120	141.2	2 47 95	.148 .158 .156	.349	2.21
,,	180	184	−2 54 96	.159 .180 .181	.335	1.86
,,	240	300	−1 50 92	.202 .262 .252	.347	1.32
,,	540	426	−2 50 93	.506 .506 .505	.414	0.82
1200s	30	20.6	6 58 90	.047 .046 .046	.395	8.59
,,	60	32.4	2 52 93	.043 .052 .049	.432	8.31
,,	120	51.6	−5 57 98	.070 .064 .061	.480	7.50
,,	300	96	2 51 97	.077 .070 .073	.487	6.96
,,	480	143	4 46 91	.101 .094 .094	.488	5.19

or near the surface of 0° C surface. The modified-phosphate coatings proved slightly more stable to simulated space environment than the "Alodine 401–45" specimen.

Farnsworth (ref. 16) of Fairchild Stratos has further developed phosphate coatings for application to detector panels on the (MMC) micrometeoroid satellite as a thermal control surface. The purpose of the MMC space vehicle is to evaluate the hazards that dust particles in space present to spacecraft in near-earth orbits. In order to optimize the statistical counting accuracy, the largest surfaces possible must be presented in the detection surfaces. The MMC detectors are large, flat-plate structures which fold out from the rocket axis and present extended surfaces. The detectors are 20-inch by 40-inch lightweight

capacitors which indicate impacts by electrical discharge through the plasma created by the hypervelocity impact. Thermal control coatings are subjected to launch aerodynamic heating, 2,000 hr minimum space exposure, and must not be so thick as to impair operation of the detector panels. Temperature limits of $+250°$ F to $-160°$ F were not too restrictive and an (α/ϵ) ratio of 1.0 was selected as being the optimum value.

Farnsworth followed Clemmons and Camp (ref. 14) and Pezdirtz and Wakelyn (ref. 15) by work using "Alodine 401–45" which suggested that a 425 mg/ft^2 coating should produce an (α/ϵ) ratio surface of 1.0. However, efforts to duplicate this coating were unsuccessful due to a decreasing adherence to the aluminum-substrate with increasing thickness. Laboratory experimentation revealed that significant improvement in the coating adherence could be obtained by increasing the phosphoric acid content and increasing the temperature to 150° F. This coating was designed as MTL–2 and gave satisfactory adherence, but for safety reasons development work continued. Further work produced the MTL–3 formulation which required further additions of phosphoric acid but permitted a reduction in bath temperature to 105° F.

The MTL–3 formulation and procedure are as follows:

Bath temperature	105° F
Immersion time	6½ min
Hydrofluoric acid	0.004 mole/l
Phosphoric acid	0.646 mole/l
Chromic acid	0.065 mole/l

Samples of 2024–T3 aluminum, measuring 2 by 2 by 0.060 inches before coating, were degreased in polyethylene equipment with trichloroethylene and then cleaned in a mild-alkaline cleaner. The MTL–3 coating was adherent to 2024, 6061, 7075, 2014, 1158, and 2024 Alclad aluminum alloys. No detrimental characteristics were noted in thermal exposure tests to 250° F, outdoor exposure, or the standard salt spray test.

Measurements of the (α/ϵ) ratio were obtained using the Dynatech Corporation apparatus. Emissivity data was secured with the Lion Research Corporation emittance device. Measurements of the (α/ϵ) and (ϵ) were made as a function of various MTL–3 process development parameters. As a function of bath temperatures from 85 to 125° F the emittance increased linearly from 0.46 to 0.66, the (α/ϵ) values decreased from 0.85 to 0.77 with all of the reduction occurring before reaching 100° F. Therefore, the derived (α) values increased from 0.40 to 0.46 in approximately a linear manner. Immersion time increased the emittance values from 0.36 at 4 min to 0.68 at 88 min and the (α/ϵ) ratio decreased nonlinearly (negative deviation) from 1.0 to 0.70 for the corresponding immersion periods. Hydrofluoric acid variations between 0.04 and 0.89

(mole/l) increased (ϵ) from 0.26 to 0.76 and decreased (α/ϵ) data from 0.96 to 0.72. Thus, process parameters are quite flexible and produce a wide range of temperature control surfaces on aluminum using the phosphate coating method with process variations.

Farnsworth, being aware of Pezdirtz and Wakelyn's work (ref. 15), performed similar ultraviolet stability tests with generally the same results, except that perhaps the increase in ratio (α/ϵ) was more rapid. Because these changes produced the high operating temperatures in the MMC vehicle, the MTL–3 coating appeared unsatisfactory due to its ultraviolet vacuum stability characteristics. However, Farnsworth suspected that the removal from the vacuum and exposure to the atmosphere for measurements contributed to the degradation, and that the increase in the (α/ϵ) ratio observed was solely a function of the ultraviolet vacuum exposure. Figure 23 shows the results of (α/ϵ) ratio obtained for intermittent exposure, indicated by the dashed line, up to the maximum value of 1.50 (starting from an initial value of 1.05) after about 500 equivalent sun hours. Then the same sample was left in place in the vacuum and further exposure given and measurements taken. The results shown by the upper solid line indicate a continued decrease in (α/ϵ) ratio down to 0.86 after approximately 300 additional equivalent solar hours exposure. The bottom curve indicates the effects of the simulated space 1×10^{-5} Torr pressure for continuous exposure. It is apparent that the change in properties does not exceed experimental error.

The exact mechanisms of changes in (α/ϵ) value because of sequential exposure to vacuum-ultraviolet and air are not clear. The most likely mechanisms concern the absorption of atmospheric gases, probably water vapor on or into the coating followed by interactions during vacuum exposure. This mechanism is being investigated in greater detail. This observation concerning ultraviolet-vacuum testing or space simulated materials testing should serve as a valuable object lesson to all those involved in testing. As a general rule, no property should be measured in the atmosphere after simulated vacuum tests; instead it should be measured in situ.

PAINTS AND PIGMENTS

The present investigations of inorganic pigments in organic and inorganic vehicles have demonstrated several advantages for temperature control coatings. Further studies offer the promise of developing fully the following potential advantages: (1) flexibility in use; (2) absence of detrimental effect on the structure of the substrate material; (3) possession of a wide variety of optical properties; (4) low cost of production; (5) ease of application and repair; (6) compatibility with a wide variety
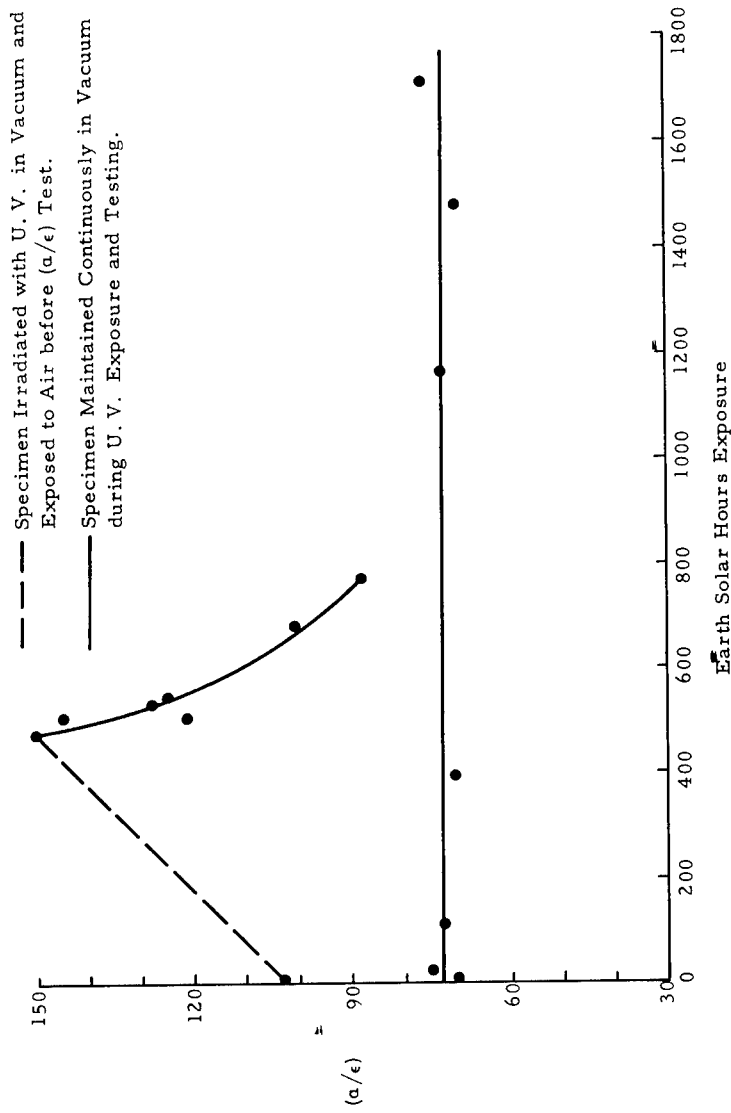
FIGURE 23.—Effect of ultraviolet irradiation and testing procedure upon the (α/ϵ) ratio of the Fairchild Aircraft MTL–3 conversion coating.

of substrates; and, (7) freedom from corrosion or alteration during prelaunch periods.

NASA sponsored the work of Zerlaut and Harada (ref. 17) on JPL Subcontract 95011 under contract NAS 7–100 which resulted in the development of three stable low solar absorptance coatings. The ultra-violet-degradation studies, reported separately, will be discussed elsewhere. The specifications of these three stable paints designated as Z93, S–13, and S–33 are as follows:

Zinc Oxide Pigmented Potassium Silicate Paint-Z93

Materials.—SP 500 ZnO was obtained from New Jersey Zinc Co. The vehicle, PS7 potassium silicate, was obtained from Sylvania Electric Products Corp. The pigment is calcined at 700° C for 16 hr (heating and cooling rates are not critical).

Formulation.—The materials are mixed in a pigment-to-binder ratio (PBR) of 4.3 to 1.0 and a solids content of 56.9 percent. A typical batch comprises 100 g ZnO, 50 cc PS7 (35 percent solution) and 50 cc distilled water. Ball-milling of the ingredients is done with porcelain balls in a dense-alumina mill. The volume ratio of balls to materials is 1:3, and the total charge is less than 50 percent of the internal volume of the ball mill. A milling time of 6 hr at 70 percent critical speed (rpm = 54.2/ $\sqrt{\text{mill radius (ft)}}$) yields a satisfactory consistency which is recommended for spraying.

The paint is prepared immediately before use. Actual shelf time should not exceed 24 hr. The mixture should be shaken occasionally to resuspend the pigment.

Application.—The formulation is applied by spray-painting. The carrier-gas should be clean; prepurified nitrogen is satisfactory. Aluminum or plastic substrates should be abraded with #60 Aloxite metal cloth, or equivalent, and then thoroughly washed with detergent and water.

The application technique consists of spraying at a distance of 6 to 12 inches until a reflection, due to the liquid, is apparent. This is followed by air-drying until the gloss is practically gone, after which the spraying-drying cycle is repeated. Since a thickness of about 1 mil is achieved per cycle, coating thickness can be predicted satisfactorily. Since hand-spraying is inherently an art and not a science, experience must be gained by the individual in developing the most satisfactory technique.

Reapplication.—The porous nature of a cured coating demands heavy spraying when applying a second coat to obtain the characteristic gloss of a satisfactory, finished texture. If the area to be repainted has been contaminated, it should be cleaned with detergent and water. If desired, the paint can be removed simply by abrasion since it is pliable.

Curing.—Satisfactory physical properties are obtained by an air-drying cure. Improved hardness is obtained by heat-curing at 140° C. Strict

adherence to cleanliness must be observed during the curing procedure. Impurities greatly decrease the stability of paints to the space environment.

Physical Properties.—The coating is porous and relatively soft. It exhibits good resistance to a thermal-shock treatment comprising immersion in liquid nitrogen followed by heating to 200° F. Z93, free of the usual brittle nature of ceramics, withstands stresses satisfactorily. Soiling tendencies, however, are high. Cleaning is accomplished with detergent and water. Acetone and similar organic solvents must be avoided because they leave a degradable residue.

Optical Properties.—Minimal solar absorptance (α) is approached at a coating thickness of 4 mils, where the predicted (α) is 0.16 $\pm$ 0.01. A thickness of 5 mils yields a minimum of 0.15 (α). For satisfactory physical properties, the thickness should be between 4 and 6 mils. Emittance (ϵ) is relatively insensitive to coating thickness, and values >0.90 can be expected at 2 mils or greater.

Stability to Ultraviolet Irradiation in Vacuum.—The severest space-simulation test to which this material was subjected was for 4200 ESH (earth sun hours), after which (α) increased by 0.014. An identical composition, which had been heated at 500° C for 2 hr in another space-simulation test, showed a gain in (ϵ) of 0.007. Thus, good stability can be expected from Z93 if it is properly prepared.

The importance of cleanliness in all aspects of handling cannot be over-emphasized. The undesirable contribution to coloration by various contaminants was clearly demonstrated in several experiments.

Zinc Oxide Pigmented Silicone Paint S-13

Materials.—The ingredients are: New Jersey Zinc SP 500 ZnO (240 parts by weight); General Electric LTV–602 silicone compound (100 parts by weight); General Electric SRC–05 catalyst (1 part by weight); and, toluene (183 parts by weight). The PVC (pigment volume concentration) is 30 percent, and the solids content is 40 percent by volume.

Formulation.—The ZnO, the LTV–602, and one-half the toluene are premixed and charged to a porcelain ball mill in a quantity sufficient to just fill the void space when the mill is half filled with grinding stones. The paint is ground for about 16 hr at approximately 70 percent critical speed. The basic charge is then removed, and the remainder of the toluene is added to the mill. The residue and the solvent are ground until the contents are uniformly thin, but for no more than 5 min. The contents are then added to the main charge and the whole mixed thoroughly. NOTE: THE SRC–05 CATALYST IS NOT ADDED UNTIL THE PAINT IS APPLIED. Borundum-fortified porcelain mills and grinding media are recommended. Cleanliness of the ball mill is essential. The formulation had excellent shelf life.

Less than 1-mil-thick layer of dried primer is required; obviously, it must adhere to the surface to which it is applied. Either General Electric's proprietary SS–4004 or SS–4044 primer can be used. A red dye in SS–4004 facilitates control of thickness during application. The use of SS–4004 rather than SS–4044 results in a solar absorptance (α) between 0.01 and 0.02 higher. The primer should be allowed to air dry for 1 hr before applying the paint.

Both S–13 and the primer are applied by spray-painting. A gas pressure of 30 to 35 psi is required when a Paasche type AUTF airbrush is used. The use of a larger gun may require experimentation with both the gas pressure and the solvent concentration. The carrier gas should be clean; pre-purified nitrogen is recommended. The SRC–05 catalyst is added immediately before application to an amount of paint no larger than that which can be applied in 20 to 30 min. The paint air-cures in 16 hr. Curing can be slightly accelerated by heating to 150 to 200° F.

Reapplication.—Soiled or damaged areas can be recoated. Soiled areas must be cleaned thoroughly with detergent and water. The surface must be dry before application of additional S–13. Damaged or gouged areas can be recoated by making a paste of S–13 in which the bulk of the solvent is omitted. The S–13 paste can be trowelled or brushed over the damaged area and cures tack-free in a few hours.

Physical Properties.—Paint S–13 is rubbery and resilient. Therefore, it can be gouged by a sharp tool with little effort. Its adherence is excellent when a primer is used, but is very poor when applied directly to a metal substrate. Without primer, it can be stripped from the substrate in one piece. Because of its resiliency, dirt tends to cling to the surface. Dirt can be easily removed by wiping with a water-moistened CLEAN, SOFT cloth. NOTE: S–13 SHOULD NEVER BE CLEANED WITH ORGANIC SOLVENT (EXCEPT AT A SACRIFICE TO STABILITY). Paint S–13 withstands more than 10 thermal-shock cycles comprising immersion in liquid nitrogen followed by rapid heating to 200° F. The paint can be torsionally stressed to 90° without failure and withstands repeated bending to 180°.

Optical Properties.—Minimal (α) is not obtained until a thickness of nearly 10 mils is reached. The following tabulation is provided as a guide.

Thickness (± 0.25 mils)	Solar absorptance (± 0.01)
1	0.33
2	.27
3	.25
4	.23
5	.22
6	.21
8	.20
9	.19
10	.19

A working range of 5 to 8 mils is recommended. For coatings of 4 mils or thicker, the total normal emittance at (200° F) is 0.90 or more.

Stability to Ultraviolet Irradiation in Vacuum.—In the most severe test to which this material was subjected for 2,400 ESH, (α) increased from 0.21 to 0.25, with $\Delta\alpha = 0.06$. Cleaning with water or with detergent and water before irradiation does not affect stability. Because cleaning with acetone severely affects stability, cleaning with water or with water and detergent is recommended.

Zinc Oxide Pigmented Paint S–33

Materials.—This paint is based on an experimental methyl-silicone resin synthesized at the IIT Research Institute. The pigment is New Jersey Zinc SP 500 ZnO. Tetrabutoxy titanium (TBT) obtainable from Du Pont is used as a cross-linking (curing) agent.

The experimental resin, R–9, is prepared as follows. Three-tenths mole (38.7 g) of dimethyldichlorosilane (99.4 percent) and 0.48 mole (72.0 g) of methyltrichlorosilane (95 percent) are mixed in 300 g of anhydrous diethyl ether. The resultant mixture is added dropwise with agitation, over a period of 40 minutes, to 1,000 g of ice. The ether layer is separated and washed with a 5-percent solution of sodium bicarbonate, followed by three washings with distilled water. The ether solution is dried over Drierite and evaporated at reduced pressure, leaving a viscous, colorless resin. This stock resin is distilled at 100 to 107° C at a pressure of 0.01 to 0.04 mm Hg in an ASCO "50" Rota-Film molecular still. The upper-molecular-weight fraction is collected as resin R–9. It should possess a molecular weight of 2,000 to 2,200, the lower limit being critical. The resin is decolorized with Darco Activated Carbon G60 obtained from the Atlas Powder Co.

The ingredients of the paint are: New Jersey Zinc SP 500 ZnO (316 parts by weight); IIT Research Institute experimental silicone resin R–9 (100 parts by weight); tetrabutoxy titanium (TBT) (1 part by weight); and toluene (225 parts by weight). The PVC is 40 percent and the solids content is 40 percent by volume.

Formulation.—The ZnO, the R–9 resin, and 100 parts of the specified toluene are premixed and charged to a porcelain ball mill in a quantity sufficient to just fill the void space when the mill is half filled with grinding stones. Borundum-fortified porcelain mills and grinding media are recommended. Shelf life is excellent. The paint is ground for about 16 hours at approximately 70 percent critical speed. The TBT is added just prior to application. The basic charge is removed and 100 parts of the toluene are added to the mill. The residue and solvent are ground until the contents are uniformly thin, but for no more than 5 minutes. The contents are then added to the main charge and mixed thoroughly. The TBT and the remaining 25 parts of the toluene are mixed together

and slowly added to the paint with agitation. Local gelation can be avoided by vigorous agitation or stirring. Shelf life is excellent.

This formulation is semiglossy when cured. A glossy paint can be made by cutting the amount of pigment required to 264 parts by weight and the toluene to 176 parts by weight. The PVC is 35 percent.

Application.—Paint S–33 does not require a primer. The surface to which it is applied must be absolutely dry and should be lightly sand-blasted, pressure-blasted, or abraded with #60 Aloxite metal cloth or equivalent. Adherence to aluminum, magnesium, and steel substrates is excellent if these surfaces are clean. Its adherence to other surfaces is unknown.

S–33 is best applied by spray-painting at a gas pressure of 30 to 35 psi when a Paasche type AUTF airbrush is used. The use of a larger gun may require experimentation with both the gas pressure and the solvent concentration. The carrier-gas should be clean; prepurified nitrogen is recommended. The paint should be allowed to air-dry for 1 to 2 hr, or until the solvent has evaporated. It should then be heat-cured for 1 to 2 hr at 300° F. Postcuring for 1 hr at 500° F results in a harder, more brittle, less glossy film which exhibits still greater stability to ultraviolet vacuum exposure.

Physical Properties.—Paint S–33 is hard and brittle. It resists soiling, particularly when pigmented at 35 percent rather than 40 percent PVC. It does not remain intact when bent 90° around a ½-inch mandrel, but does withstand torsional stress to 90°. It withstands 10 cycles of thermal-shock treatment comprising immersion in liquid nitrogen followed by rapid heating to 200° F. Cleaning can be accomplished by washing with a detergent followed by copious quantities of distilled water. Since the effect of cleaning with organic solvents is unknown, their use is not recommended.

Optical Properties.—Minimal solar absorptance (α) is reached at a thickness of approximately 7 mils. The following tabulation is provided as a guide.

Thickness (± 0.25 mils)	Solar absorptance (± 0.01)	Total normal emittance (200° F
1	0.29	0.80
2	.25	.88
3	.23	.89
5	.205	.90
6	.20	.91
7	.195	.92

A working range of 3 to 5 mils in thickness is recommended. The emittances listed are estimates based on data which showed considerable scatter.

Stability to Ultraviolet Irradiation in Vacuum.—The severest test to which paint S–33 was subjected was for 4,200 ESH. A specimen of S–33 which was cured for 1 hr at 300° F increased 0.020 in (α), whereas a specimen postcured for 1 hr at 500° F increased 0.011 in (α). The paint if pigmented at only 35 percent PVC, is somewhat less stable, and (α) may increase 0.02 after 2,000 ESH exposure.

Working under NASA Contract NAS 7–100, Subcontract No. 950056, Blair (ref. 18) of the Hughes Aircraft Company developed a pigment for thermal control paints comprising a trivalent-metal silicate dispersed in a potassium silicate vehicle. The aluminum silicate used, a white clay, was pretreated by heating in air for 1 hr at 1,275° C in thin layers. The fired clay was milled with water into a ceramic slip and then mixed with the vehicle. The particular value of this pigment is its low solar absorptivity ($\alpha = 0.13$) and high emittance ($\epsilon = 0.93$) giving an (α/ϵ) ratio of 0.14. Moreover, this coating is resistant to ultraviolet exposure in vacuum.

Zerlaut, Tompkins, and Harada of the IIT Research Institute working under NASA Contract NAS 8–5479 for the Marshall Space Flight Center are pursuing a number of different procedures to increase the solar reflectance of zinc oxide-pigmented, potassium silicate and methyl-silicone paints (ref. 19). Attempts are being made, by the introduction or creation of microbubbles in the paint vehicles, to increase light scattering (reflectance). Mechanical agitation to produce emulsions, the addition of bubble-forming agents which change their physical state during forming, and chemical methods of bubble formation are being investigated.

The results obtained to date represent the first efforts. No suitable coating has been developed to date, although several systems have produced porous films. A silicone resin (R–5), (an experimental methyl-silicone-material prepared by IIT), was foamed by the addition of tetrabutoxy titanium (TBT) dissolved in methylene chloride. The best procedure found was spraying the resin with an air brush and TBT on a heated glass plate. A 30 percent (by volume) solution of the resin and a 10 percent TBT solution in methylene chloride were used in a 1:1 mixture and sprayed onto glass slides held at 150° C. Measurements on the translucent layer indicated that a reasonable bubble structure was obtained, although the bubbles were too large. Experiments were continued.

NASA Contract NAS 8–1532 with Anderson Chemical Division of Stauffer Chemical Company developed a film-forming polymer which is essentially inorganic and possesses excellent resistance to heat and vacuum-ultraviolet degradation (ref. 20). Silicones having the basic chain polymer structure (–O–Si–OSi–) are cured by the action of small

additions of tetrabutoxytitanium (TBT). The curing action is believed due to linkages of the type (–Ti–O–Si–O). Since these titanium-modified paints exhibited improved space application characteristics, a contract was awarded to conduct a systematic study of the film-forming polymers of the silicone type containing increased amounts of titanium and related metals.

In order to prepare polymers having the basic chain structure (–Ti–O–Si–O–), the contractor found it necessary to synthesize compounds having the structure $Ti(NR_2)_2(OSiR_3)_2$, where R is (normally) a small alkyl group and R' may be an alkyl or aryl group. Three possible methods for the preparation of these bis-dialkylamino-bis-trialkyl(ary)siloxy-titanium compounds were considered. These were:

1. $Ti(NR_2)_4 + Ti(OSiR_3)_4 _____ 2\ Ti(NR_2)_2(OSiR'_3)_2$
2. $Ti(NR_2)_4 + 2\ R'_3SiOH _____ Ti(NR_2)_2(OSiR'_3)_2 + 2\ R_2NH$
3. $TiCl_2(NR_2)_2 + 2\ NaOSiR'_3 \_\_\_ Ti(NR_2)_2(OSiR'_3)_2 + 2NaCl$

Reaction 1 was attempted by refluxing the two materials in benzene for 10 hr. Only unchanged starting materials were recovered.

Reaction 2 was attempted using triphenyl silanol and tetrakisdimenthylaminotitanium. The product consisted of a mixture of three materials, and it was apparent that separation of the desired product would be difficult.

Reaction 3 was found to be entirely satisfactory for the preparation of the desired compound. Separation from the byproduct sodium chloride was accomplished by high-vacuum distillation. This method of synthesis was successful in preparing analogous aluminum compounds.

Although some of these materials have been used in the preparation of polymers, the suitability of the polymers for the purpose intended has not been fully determined.

EXAMPLE OF AN INORGANIC PIGMENT USED ON A SATELLITE

The NASA Explorer IX satellite (ref. 21) (fig. 24) was a rigid sphere 12 ft in diameter, weighing 14.62 lbs. Its purpose was to measure the density of space and other drag forces acting on a uniform, low density object. The weight per unit of frontal area was 0.1292 lb/ft². The 4-layer laminate had to be lightweight, easily visible for tracking, and pliable enough to allow folding and reopening without separation of the four layers. The aluminum foil had an (α/ϵ) ratio so high that some means had to be used to keep the orbital temperatures below the level destructive to the polyester film. The orbital temperatures were held to a satisfactory level by covering 18 percent of the exterior surface of the 4-layer laminate with low (α/ϵ) titania-(rutile) pigmented-epoxy paint in a uniform polka-dot pattern.
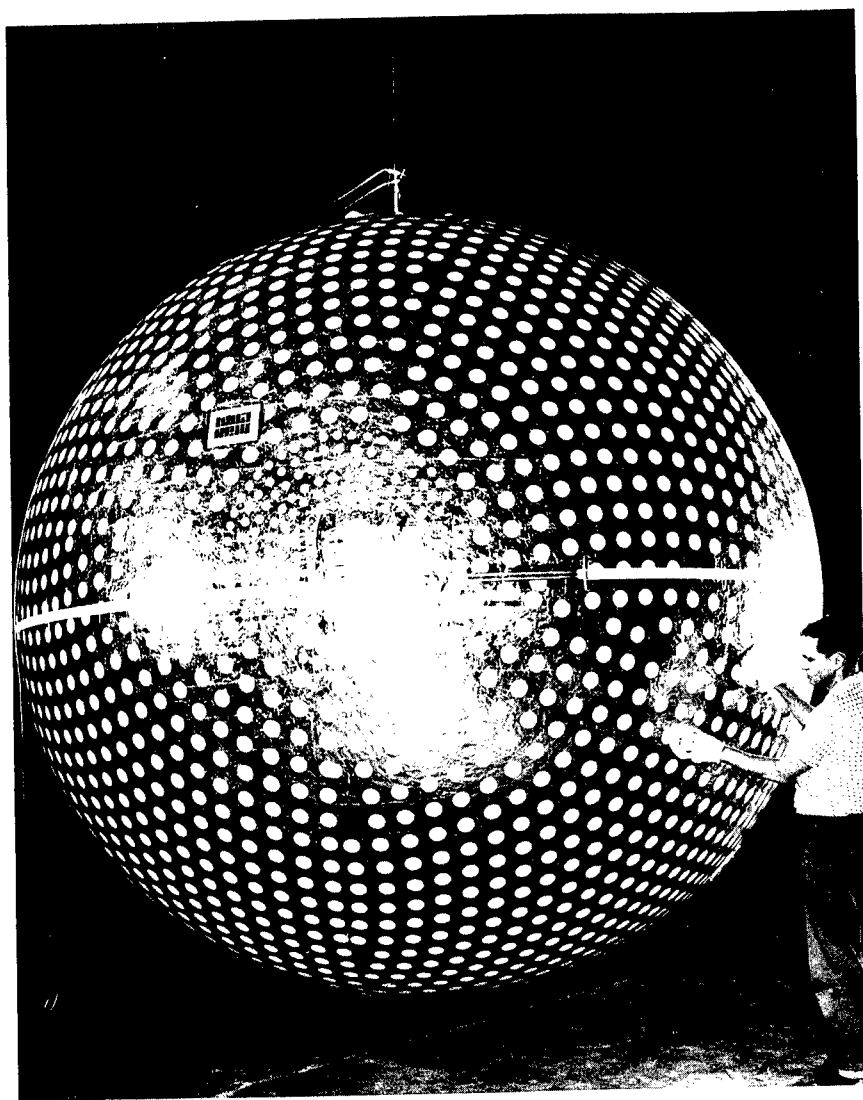
FIGURE 24.—NASA Explorer IX.   A 12-foot diameter inflatable spherical satellite covered with 3,600, 2-inch diameter white dots for temperature control.

The thermal control required must be lightweight, provide a highly visible satellite for tracking, and be sufficiently adherent to allow folding and reopening.   The aluminum foil as previously cited has an (α/ϵ) ratio that results in orbital temperatures higher than that to which the polyester film should be subjected, therefore low (α/ϵ) TiO_2 (Rutile) pigmented epoxy paint was used to cover 18 percent of the exterior surface in a uniform polka-dot pattern.

RESPONSE OF COATINGS TO THE SPACE ENVIRONMENT

Space environmental hazards which are most likely to affect the properties of coating are: (1) vacuum $\sim 10^{-15}$ Torr; (2) solar ultraviolet photons; (3) solar protons; and, (4) micrometeorites. Of these, the most serious, particularly for paints and pigments, are the combination of vacuum and ultraviolet radiation. While the necessity for continued and accelerated work remains, enough initial information is currently available to ascertain the general magnitude of problems associated with the alteration of optical properties of materials in response to space environmental factors.

Ultraviolet Degradation

An extensive study of the ultraviolet irradiation effects upon inorganic pigments and organic and inorganic vehicles has been undertaken by Zerlaut, Harada, and Thompkins (ref. 22) on JPL Subcontract 95011 under NASA Contract NAS 7-100 at the IIT Research Institute. The reflectance and solar absorptance of a broad group of inorganic materials was determined before and after exposure to vacuum ultraviolet irradiation. The results of this general screening test (table 7) indicate that the thermally stable oxides are not necessarily the most stable to ultraviolet irradiation. Because ZnO proved particularly stable as a material, a number of different oxides from various sources were tested. The results (table 8) indicate that zinc oxide is a markedly stable material under ultraviolet irradiation. Also, ZnO's low, absolute solar absorptance makes it a particularly promising pigment for stable-white coatings. Of the inorganic materials, zinc sulfide, stannic oxide, and Molochite (a highly calcined aluminum silicate made from high-purity kaolin) possessed good ultraviolet resistance.

Water-based inorganic vehicles such as monaluminum dihydrogen phosphate, colloidal silica, and alkali silicates were investigated. The alkali silicates proved to be superior both from the standpoint of ultraviolet stability and general physical properties. Three other classifications of binders were evaluated: (1) commercially available silicones; (2) fluorine-containing aliphatic resins; and, (3) a modified silicone-epoxy composition. Many combinations of zinc oxide-pigmented paints also were made.

The results of the most severe test, made at 4,170 ESH duration at 10.6 suns intensity which corresponds to nearly 6 months of direct extraterrestrial ultraviolet irradiation, are shown in table 9 for potassium silicate-zinc oxide paints. These results show that the 500° C heat treatment is beneficial as is an increasing pigment-to-bond (PBR) ratio. The 4,170-ESH test exposure results for four zinc-pigmented methyl silicone paints are given in table 10. The specimen of S-33 when heated to 500° F for 1 hr showed the greatest stability. This paint compared

very favorably with the potassium silicate paints. The silicone increased $\Delta\alpha$ + 0.11, or 4.6 percent and the potassium silicate 0.008 or 5.5 percent. The potassium silicate paint also possessed the lowest solar absorptance $\Delta\alpha$ = 0.147 versus α = 0.237 for the methyl silicone paint. On the basis of these results, both paints appear very stable with the potassium silicate having a slight advantage.

The exact mechanisms of ultraviolet degradation in pigments, vehicles,

TABLE 7.—*Effect of Ultraviolet Irradiation in Vacuum on Optical Properties of Miscellaneous Inorganic Pigments*

Material	Manufacturer's designation	Exposure		Reflectance, %	
		ESH	Solar factor	440 mμ	600 mμ
Al_2O_3	Alucer MC (alpha), Gulton Industries.	0 180	3	100.0 74.0	100.0 91.5
Al_2O_3	Alucer MA (gamma), Gulton Industries.	0 75	1.5	93.5 49.5	90.0 82.5
$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.	Ajax P Kaolin, Georgia Kaolin.	0 180	3	73.0 46.5	84.5 60.0
$Al_2O_3 \cdot 2SiO_2$	Ajax SC Kaolin, Georgia Kaolin.	0 200	3	78.0 65.0	87.0 81.0
$3Al_2O_3 \cdot 2SiO_2 + SiO_2$.	Molochite, Paper Makers Importing Co.	0 180	3	84.5 75.5	86.5 84.5
Sb_2O_3	National Lead Co.	0 75	1.5	92.5 36.5	96.5 50.0
$CaSiO_3$	Synthetic, Johns-Manville.	0 75	1.5	86.0 58.0	90.0 81.0
$CaSiO_3$	Wollastonite C–1 Cabot	0 75	1.5	92.5 81.0	94.5 91.5
$MgAl_2O_4$	Spinel, Linde	0 75	1.5	97.5 70.0	97.0 92.5
MgO	Reagent-grade powder, Mallinckrodt.	0 75	1.5	98.5 71.0	98.5 92.5
$MgSiO_3 \cdot nH_2O$	No. 140 Alabama talc, Whittaker, Clark and Daniels.	0 180	3	89.0 62.0	92.0 73.5
$2MgO \cdot SiO_2$	AlSiMag 243, American Lava.	0 1,036	15	33.0 35.5	59.0 60.0
Magnesium trisilicate.	USP, Mallinckrodt	0 200	3	97.5 18.5	99.0 44.5
SiO_2	Ottawa Special, Ottawa Silica.	0 75	1.5	88.5 77.5	92.5 90.0
SiO_2	Diatomaceous earth, Dicalite WB–5, Great Lakes Carbon.	0 180	3	92.0 87.5	93.5 93.0
SnO_2	CP, Fisher	0 300	3	88.0 78.5	90.0 88.0
ZrO_2	CP, Titanium Alloy Mfg.	0 75	1.5	92.5 65.5	97.0 90.5
ZrO_2	Cubic, Titanium Alloy Mfg.	0 180	3	88.0 33.0	95.5 73.5
$ZrSiO_4$	Superpax Titanium Alloy Mfg.	0 180	3	86.5 65.0	92.5 84.5
ZnS	Reagent grade, Matheson, Coleman and Bell.	0 75	1.5	91.0 89.0	94.5 94.0

TABLE 8.—*Effect of Ultraviolet Irradiation in Vacuum on Optical Properties of Zinc Oxide Pigments*

Manufacturer's designation	Particle size, μ	Purity %	Exposure		Reflectance, %		Solar absorptance	
			ESH	Solar factor	440 mμ	600 mμ	α	Δα
SP 500	0.30	>99.90	0		95.0	99.0	---	---
			75	1.5	95.0	99.0	---	---
AZO–66	0.20	99.80	0		93.0	99.0	---	---
			200	3	91.0	98.0	---	---
USP 12	0.30	99.80	0		93.5	98.0	---	---
			300	3	92.0	97.5	---	---
AZO–33	0.20	99.20	0		88.0	95.0	---	---
			300	3	86.5	93.5	---	---
SP 500	---	---	0		95.0	99.0	---	---
			3,100	10	91.0	98.0	---	---
SP 500	---	---	0		93.5	98.0	0.138	
			1,720	10.2	90.5	96.0	.164	0.026
SP 500 (Calcined 16 hrs. at 700° C)	0.40	---	0		92.5	97.5	.133	
			1,720	10.2	91.5	97.5	.140	.007
AZO–55LO	---	99.20	0		86.5	93.5	.198	
			1,720	10.2	83.5	92.0	.213	.015
AZO–55LO (Calcined 16 hrs. at 700° C)	---	---	0		90.0	95.5	.156	
			1,720	10.2	88.5	95.9	.164	.008

TABLE 9.—*Effect of 4170 ESH of Ultraviolet Irradiation in Vacuum on Optical Properties of Inorganic Zinc Oxide Coatings. All samples cured by air drying.*

Sample	Composition*		Treatment	Exposure	Solar absorptance			
	PBR	Solids content, %		ESH	α_1	α_2	α	$\Delta\alpha$
Z93-----	4.30	56.9	Stored in air, between sheets of vellum, for 37 days.	0	0.102	0.063	0.165	
				4,170	.120	.059	.179	0.014
Z94-----	5.31	58.5	Stored in air, between sheets of vellum, for 21 days.	0	.096	.051	.147	
				4,170	.106	.049	.155	.008
Z95-----	4.30	56.9	Stored in air, between sheets of vellum, for 36 days; washed with detergent and water; air-dried for 1 day.	0	.100	.061	.161	
				0—washed	.098	.049	.147	−0.14
				4,170	.122	.050	.172	.025
Z96-----	4.30	56.9	Stored in air, between sheets of vellum, for 24 days; heated at 500° C for 2 hr; stored in air for 13 days.	0	.102	.064	.166	
				0—heated	.101	.058	.159	−.007
				4,170	.109	.057	.166	.007

* The pigment was SP 500 calcined at 700° C/16 hrs. The binder for all samples was PS7.

TABLE 10.—*Effect of 4170 ESH of Ultraviolet Irradiation in Vacuum on Optical Properties of Silicone Paints*

Paint No.	Composition			Exposure		Solar absorptance			
	Binder	PVC, %	Cure	ESH	Solar factor	α_1	α_2	α	$\Delta\alpha$
S-13	LTV-602	30	16 hr at room temperature_	0		0.124	0.087	0.211	
				4,170	10.6	.160	.109	.269	0.058
S-31	R-8	40	1 hr at 300° F_____	0		.145	.137	.282	
				4,170	10.6	.165	.151	.316	.034
S-33	R-9	40	1 hr at 300° F_____	0		.119	.097	.216	
				4,170	10.6	.128	.108	.236	.020
			1 hr at 300° F_____	0		.128	.109	.237	
			+ 1 hr at 500° F_____	4,170	10.6	.134	.114	.248	.011

and paints is still the subject of active study. Most of this and other research work have been attempts to identify the best available off-the-shelf materials. It is reasonable to expect that the identification of specific reactions and interactions of the most stable paints will be intensely studied in the near future. Once this data is known, it is probable that more sophisticated temperature control paints will be developed for space vehicles.

Proton Sputtering

Dr. Wehner (ref. 23) reported on work supported by NASA contract NASw-751 concerning the effects of the solar wind bombardment on surfaces in space. Although the specific research goal was to study proton modifications of the lunar surface this investigation produced significant results relating to spacecraft coatings. Solar proton sputtering was found to remove about 1 Å per year for copper and about half this rate for iron and oxides. However, sputtering not only removes material but it also produces chemical effects. Oxides of the non-transition elements yellow slightly due to the greater loss-of-oxygen producing defects. Black CuO is first converted to red Cu_2O, then to a film of Cu. Fe_2O_3 is converted to Fe_3O_4, FeO, and Fe under ion impact. Tin and protons combine to produce volatile SnH_4 resulting in a large apparent sputtering rate. These studies indicate that the alteration of optical properties is likely to be an area of further study, particularly for ionic-solid-inorganic-pigmented coatings.

Anderson (ref. 24), NASA Ames Research Center, has studied the effects of ion bombardment on the optical properties of metals. Three materials were selected for test: titanium alloy containing 6 percent Al,

and 4 percent V; 99.99 percent pure aluminum; and electrolytic copper. While these materials are useful as structural materials, the results are helpful in drawing conclusions concerning metallic coatings.

Polished specimens were exposed to cathode sputtering by hydrogen ions at 1,000 electron volts. Sample temperatures were held near 75° F by cooling. Emittance measurements were made on the samples before and after sputtering. After sufficient emittance data were accumulated, the specimen was repolished and resputtered for various lengths of time, while at intervals additional reflectance measurements were made.

Reflectance measurements were made at 50 points in the wavelength region 0.3 to 3.0μ. These points were selected to represent 2 percent increments of the solar spectrum in space. Total hemispherical emittance measurements were obtained by the calorimetric method. Data was obtained at 100° C.

The effect of 10^{21} ions/cm² on the spectral absorptance of pure aluminum is shown in figure 25. In the 0.3 to 0.7 wavelength region the absorptance was increased by approximately a factor of two. The effects were slightly less at the longer wavelength (0.9μ). The alteration of solar absorptance of pure copper, aluminum, and titanium alloys as a function of the number of incident ions is shown in figure 26. The (α/ϵ) ratio change is given in figure 27. The effect of these changes in (α/ϵ) ratio on the equilibrium temperature of a spherical isothermal satellite, with no internal power dissipation, is shown in figure 28. The temperature changes resulting from 10^{21} ions/cm² is important to space-vehicle designers. The density of protons in space in a quiet sun period is approximately 10^{9} protons/cm²/sec. During solar storms the intensity may increase to 10^{12} protons/cm²/sec. Thus the full exposure 10^{21} ions/cm represent about 30 years of continuous, solar maximum exposure. Polished surfaces probably undergo the maximum alteration during exposure.

Micrometeorite Impact

Merrill (ref. 25) of the Research Projects Laboratory, Marshall Space Flight Center, reported on an analytical model which was developed to predict the change in emittance of a surface caused by particle impact. This model was concerned with the increased emittance of a surface due to the formation of hypervelocity-impact craters under micrometeorite bombardment. While this paper deals only with the case of homogeneous materials it can easily be altered to study coated materials. The current assessment of this space hazard suggests that impacts of micrometeorites over a period of years are not likely to greatly affect satellite temperature coatings.
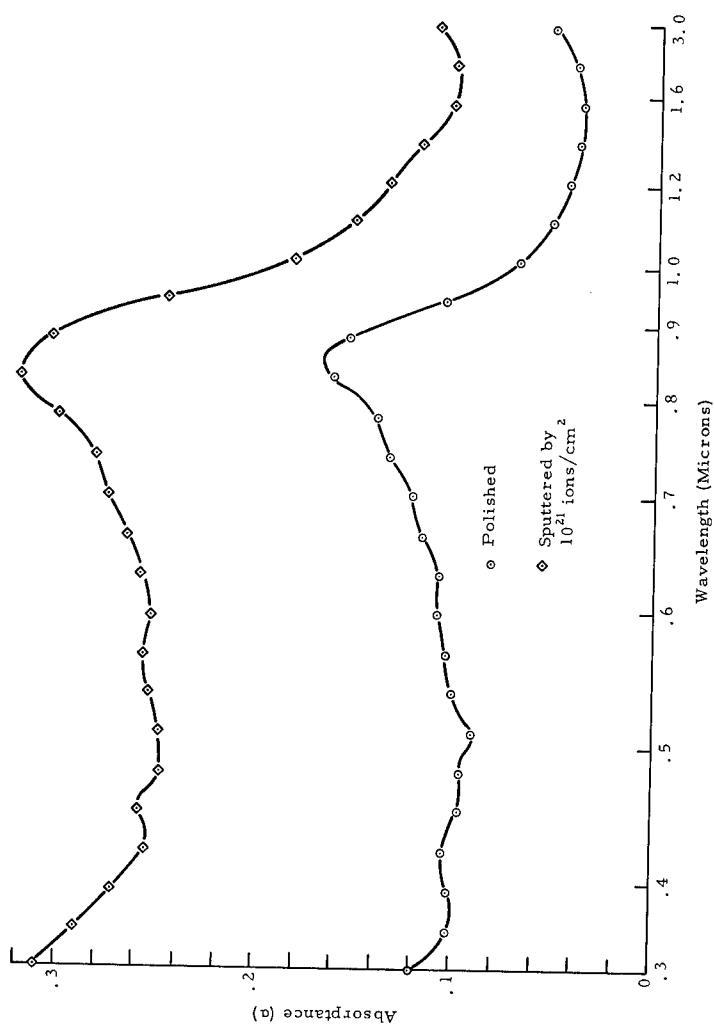
FIGURE 25.—Effect of hydrogen ion bombardment on the spectral absorptance of pure aluminum.
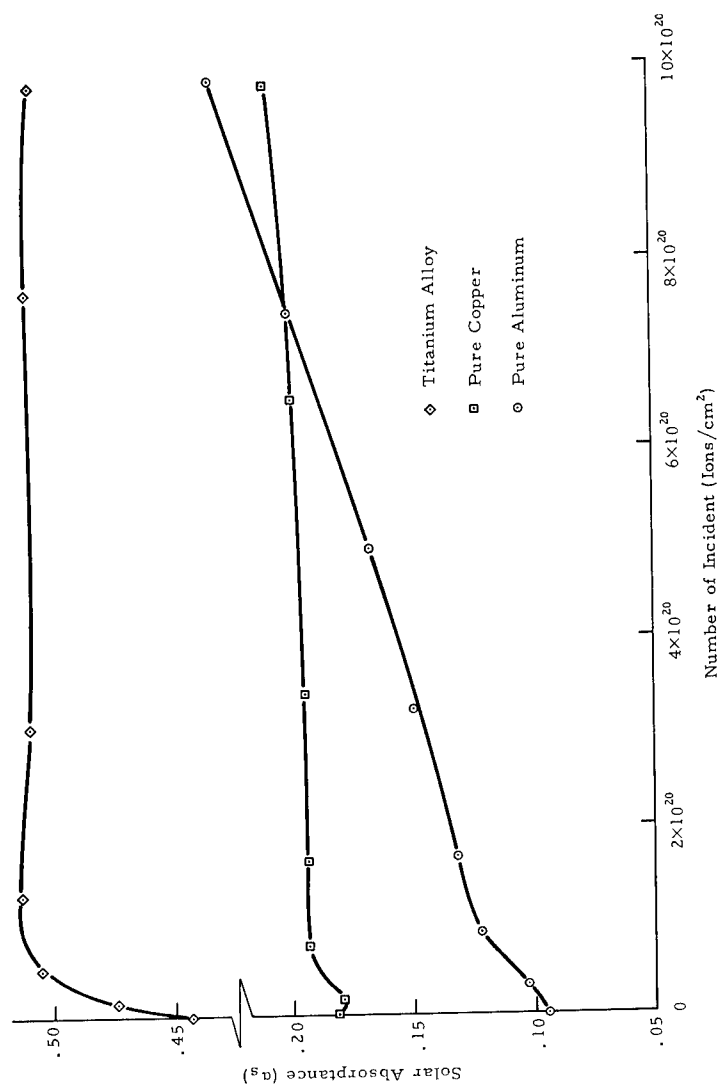
FIGURE 26.—Effect of hydrogen ion bombardment on solar absorptance of metals.
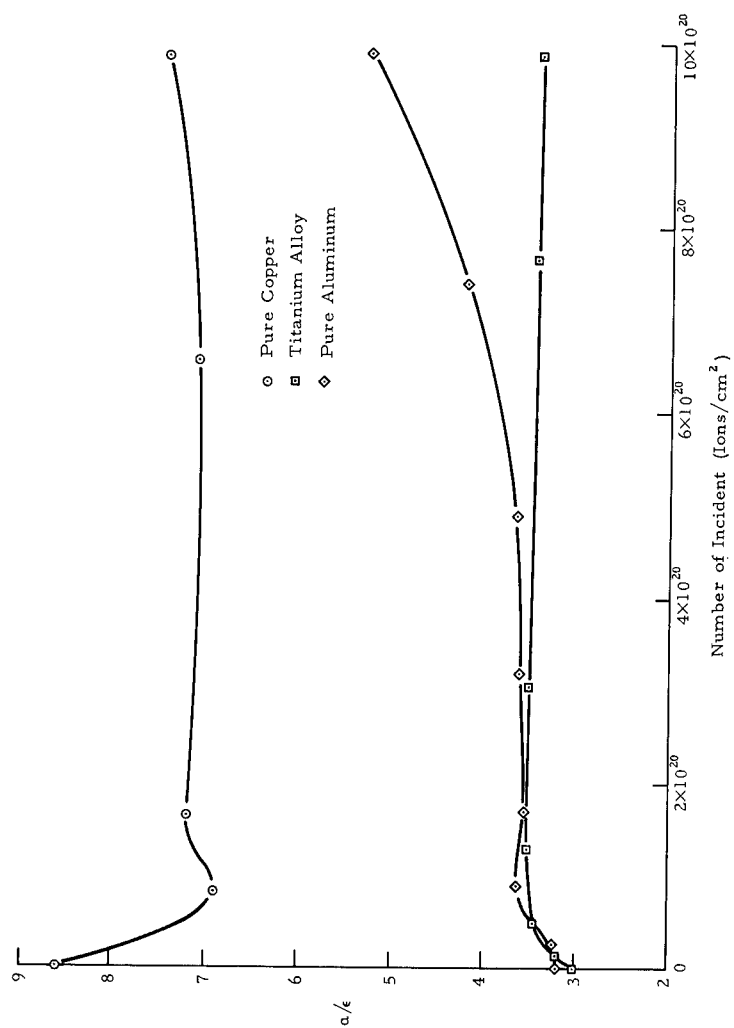
FIGURE 27.—Effect of hydrogen ion bombardment on the α/ϵ ratio of metals.
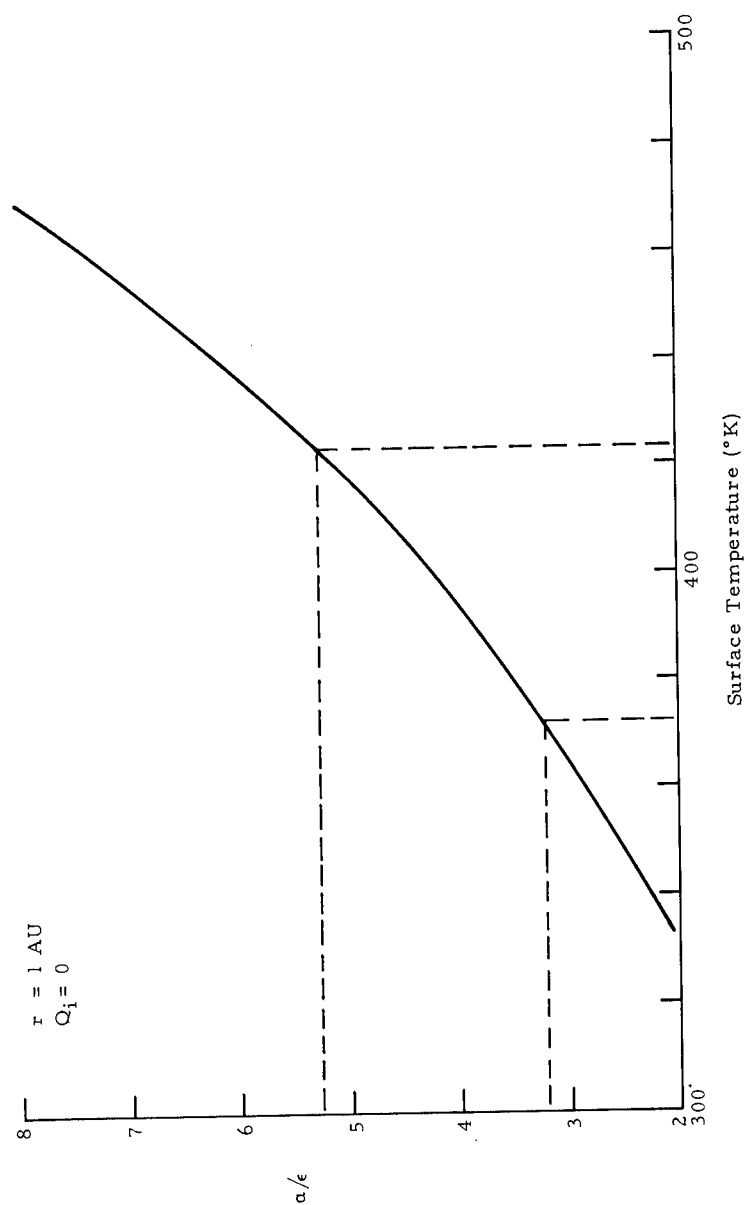
FIGURE 28.—Effect of α/ϵ ratio on the equilibrium temperature of a spherical satellite.

Testing of Temperature Coatings in Space

Some laboratory test data has been available to a rather limited extent, but space service data for long term exposure has been extremely inadequate. In several cases, satellites have carried sensors to measure temperatures to provide the first useful information. Specially designed experiments to test the performance of temperature control coatings in space as a check against laboratory data are urgently needed.

The first experiment of this type was designed and carried out by Carr B. Neel (ref. 26), NASA Ames Research Center. The satellite used for this experiment was the S–16 Orbiting Solar Observatory launched March 7, 1962. The S–16 satellite on which the experiment depended is shown in figure 29. The satellite has two main parts: a lower section consisting of a nine-sided wheel, with three attached arms, that rotates to provide gyroscopic stabilization; and a stabilized semicircular upper section, called a sail, which is aimed at the sun and contains experimental apparatus for spectroscopic solar studies in the ultraviolet region. The radiation sensor plate for the coatings test experiment was mounted on the rotating wheel just below the left center of the foreground and appears as a black, round plate with seven small circular plates clustered together. The wheel rotates at 30 rpm.

The test surfaces prepared by different organizations were selected to test as representative a sample of coatings as possible. Six coatings and
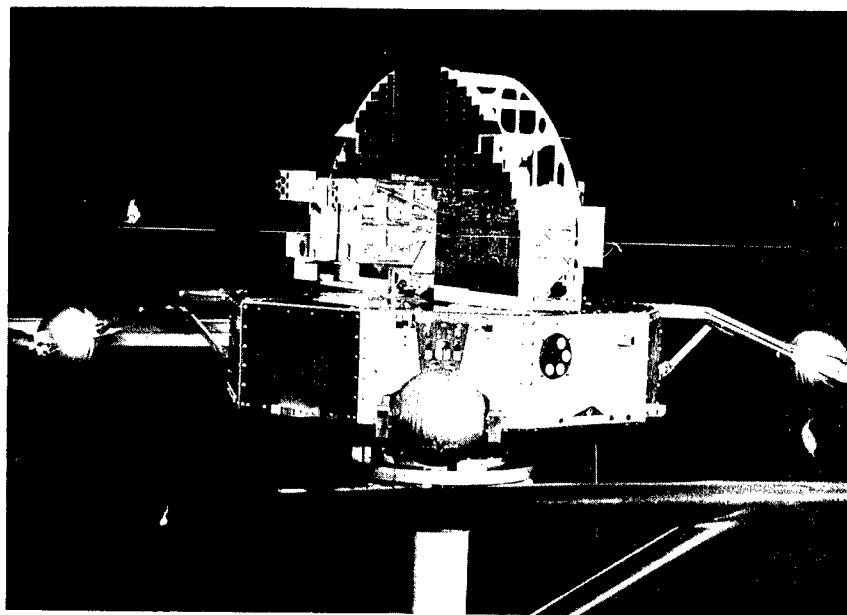
FIGURE 29.—S–16 orbiting solar observatory with sensor plate installed on rim panel.
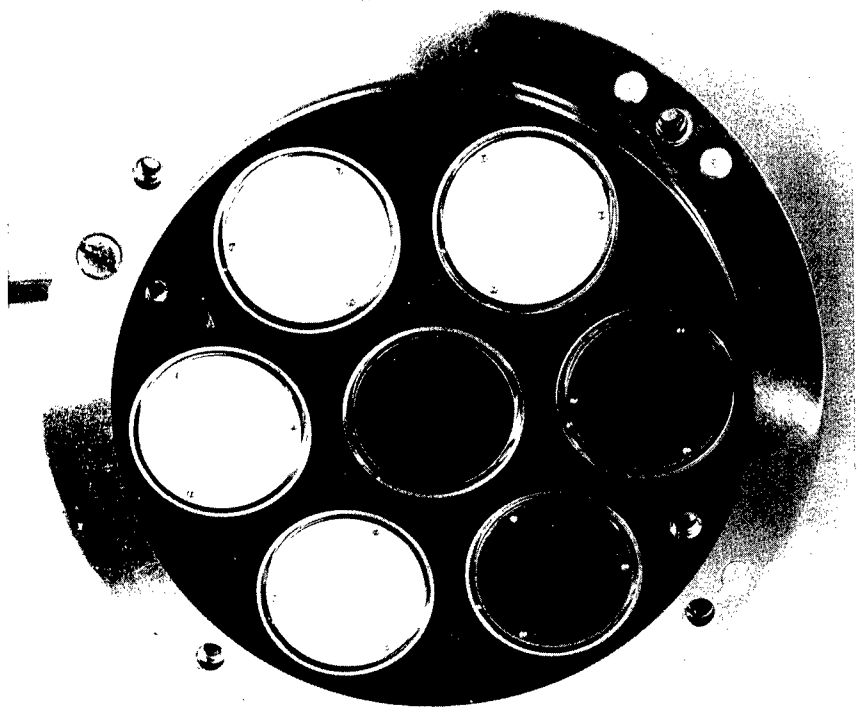
FIGURE 30.—Radiation sensor plate for S-16 orbiting solar observatory.

a blackbody reference were tested. Figure 30 illustrates the four white coatings and the two gray-appearing coatings which are special interference, vapor-deposited-layer coatings. A detailed description of each coating is given in table 11. General background information for each is as follows:

1. The first is a catalyzed-epoxy white paint which has been used by the Lockheed Missiles and Space Company on the Discoverer series of satellites. Laboratory tests indicate that this paint is quite susceptible to degradation by ultraviolet irradiation. Flight verification of this property was desirable to provide a check on laboratory tests..

2. The second coating is a TiO_2-opacified silicone paint developed at the NASA Marshall Space Flight Center and is believed to be a relatively stable white paint which can be easily applied without heating.

3. The third coating is a porcelain enamel fired at 1,000° F onto an aluminum substrate. This coating was developed by the Ferro Corporation of Cleveland, Ohio for the NASA Marshall Space Flight Center. This coating is relatively difficult to apply to spacecraft; however, it is expected to be an extremely stable coating.

4. Coating number four was developed at the NASA Goddard Space Flight Center. This coating has an (α/ϵ) ratio of about unity, and both (α) and (ϵ) have low values. This coating will maintain a satellite at or near room temperature. Furthermore, the low values of solar absorptance and emittance should decrease temperature fluctuations in passing in and out of the earth's shadow.

5 and 6. These two coatings were of a special-layered construction devised by Dr. Georg Hass of the Army Engineer Research and Development Laboratory, Fort Belvoir, Virginia, to test the erosion rate of silicon monoxide films. Silicon monoxide was used on the Vanguard satellites and is frequently used as a coating for the protection of aluminized surfaces in optical apparatus. Alternate layers of germanium and silicon monoxide were deposited with the germanium layer being the outermost surface on specimen No. 5 and silicon monoxide the outer layer in specimen No. 6. This design was developed since it was expected that the thin, 110Å-thick germanium outer layer on surface No. 5 would erode away rapidly. Germanium has a high (α/ϵ) ratio, and the under layer silicon monoxide a low ratio. Coating No. 6 possessed a 500Å-thick silicon monoxide layer over a 200Å-thick germanium sublayer. The difference in time between the drop in temperature of coating No. 5 and that of coating No. 6 would indicate the lifetime of the 500Å-thick layer of silicon monoxide. By comparison, if the silicon monoxide film were placed directly upon an aluminum substrate, at least ten times as long a period of time would be required to give comparable temperature changes. This was a very sensitive temperature-dependent system to detect surface erosion rates of semiconductor and ionic surfaces during space exposure.

The solar absorptivity (α) and emissivity (ϵ) and the (α/ϵ) ratio of all surfaces were measured in the laboratory. The solar absorptance versus wavelength for the five surfaces and the reference blackbody are given in figures 31 through 37.

The effect of ultraviolet degradation studies for all six surfaces is given in figures 38 through 40.

The test surfaces were mounted into a radiation sensor of the type shown in figure 41. This design provided a high degree of thermal isolation from the spacecraft structure. The temperature sensor was a thermistor mounted directly on the undersurface of the test specimen. Assembly of these test specimens around the blackbody reference is shown in figure 42. The details of the telemetry equipment were given by Neel (ref. 27), and since they are not relevant to coatings they will not be detailed.

The results of the S-16 experiment are particularly interesting since data was obtained over a period of 16 months. Initial values of (α/ϵ), (α), and (ϵ) obtained from flight data are compared with laboratory

TABLE 11.—*Test Surfaces*

Surface	Identifying characteristics	Source	Coating thickness, in.	Substrate material
1. TiO_2 in epoxy	A 423 Skyspar natural-white enamel	Andrew Brown Paint Co., applied by Ames Research Center	0.007	6061 T-6 aluminum alloy.
2. TiO_2 in silicone	Air-drying white paint	Marshall Space Flight Center	.002	Do.
3. White porelain enamel	Alkali-titania boro-silicate glass	Ferro Corporation through Marshall Space Flight Center	.0025	Do.
4. Aluminum powder in silicone	Leafing-type pigment	Goddard Space Flight Center	.001	Do.
5. Al-SiO-Ge[a]	Evaporated films	AERDL through Goddard Space Flight Center	See footnote	321 stainless steel
6. Al-SiO-Ge-SiO[b]	Evaporated films	Do.	See footnote	Do.
7. Razor-blade reference	Specially-constructed surface	Ames Research Center	----	----

[a] Composition of surface 5: layered construction; polished stainless-steel substrate, followed by opaque aluminum, 1.1 microns SiO, 110 A Ge (top layer).

[b] Composition of surface 6: layered construction; polished stainless-steel substrate, followed by opaque aluminum, 1.1 microns SiO 200 Å Ge, 500 Å SiO (top layer).
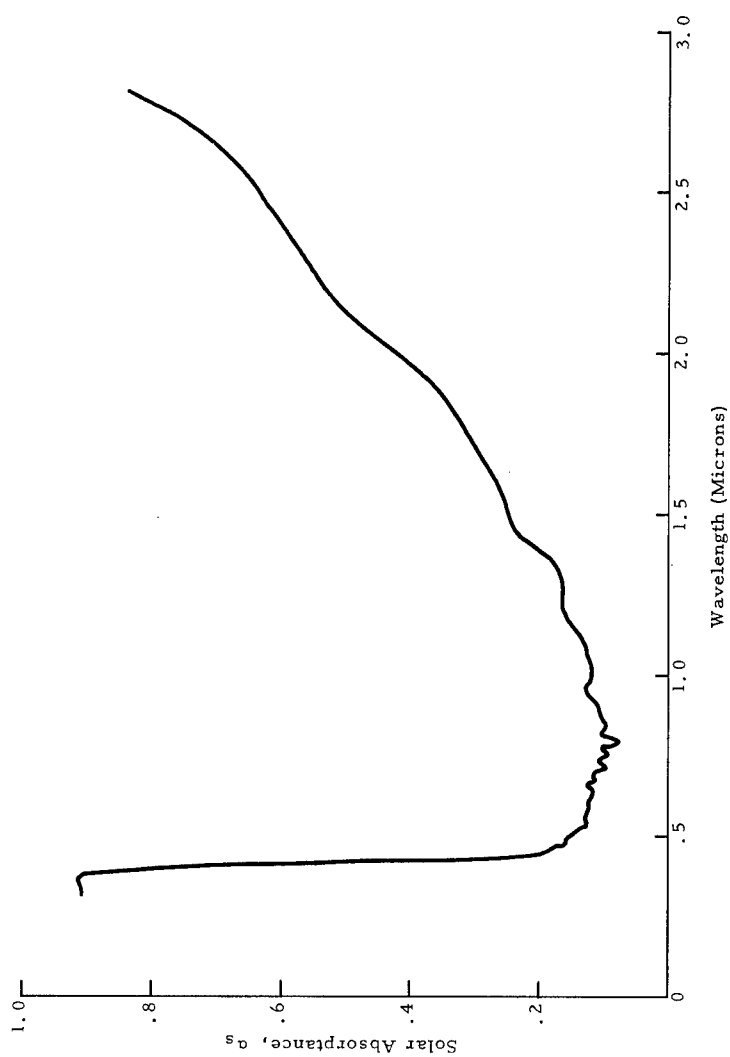
FIGURE 31.—Spectral dependence of solar absorptance.   (a) Surface 1, TiO_2 in epoxy.
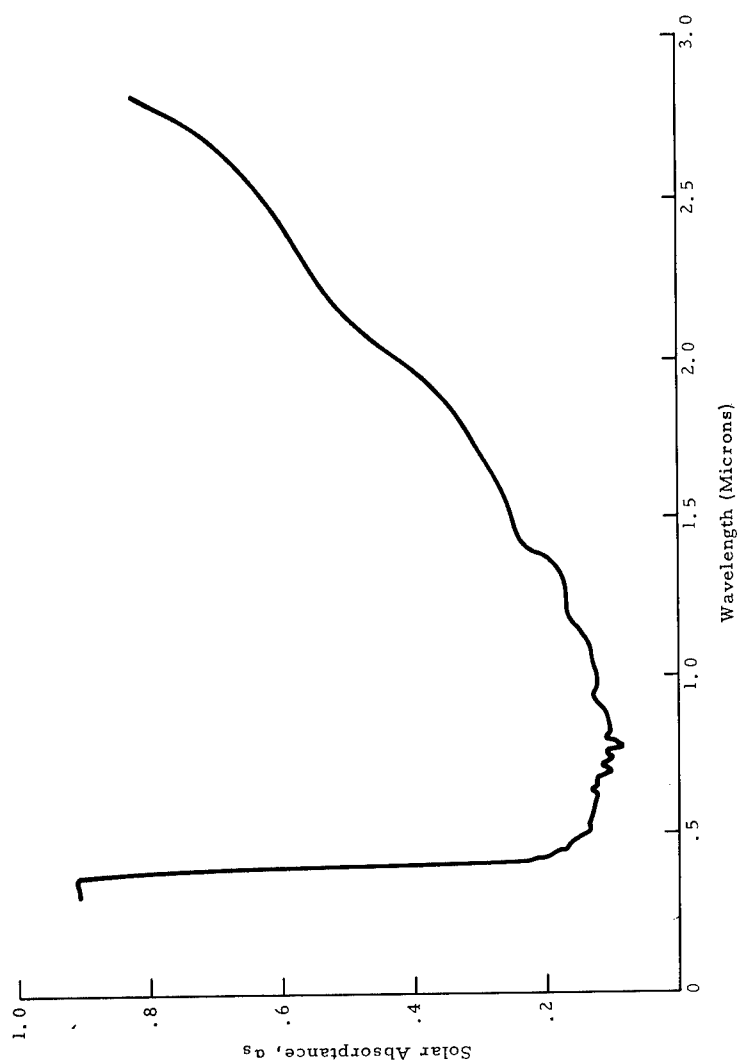
FIGURE 32.—Spectral dependence of solar absorptance. (b) Surface 2, TiO₂ in silicone.

FIGURE 33.—Spectral dependence of solar absorptance.   (c) Surface 3, white porcelain enamel.
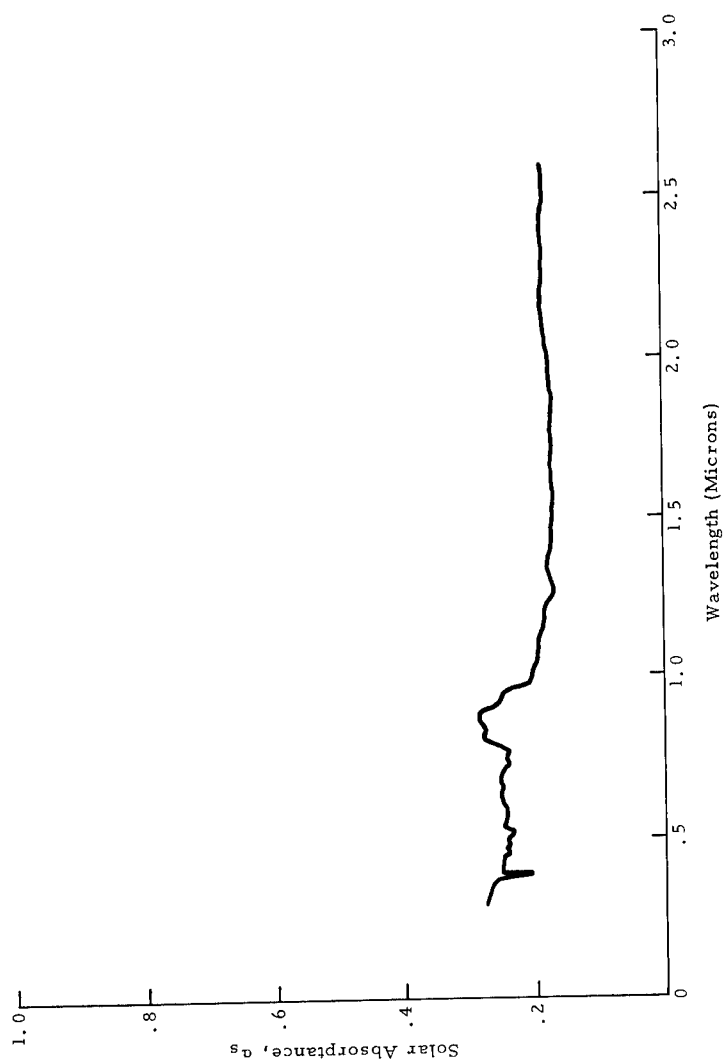
Figure 34.—Spectral dependence of solar absorptance.   (d) Surface 4, aluminum powder in silicone.
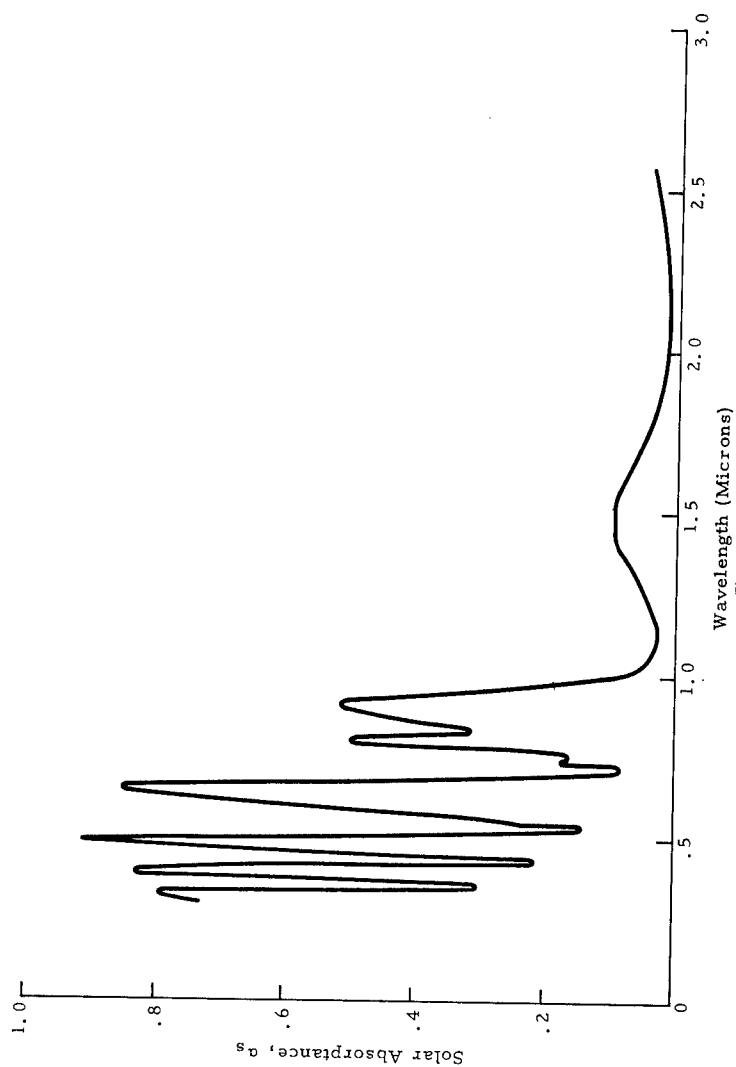
FIGURE 35.—Spectral dependence of solar absorptance.   (e) Surface 5, Al-SiO-Ge.
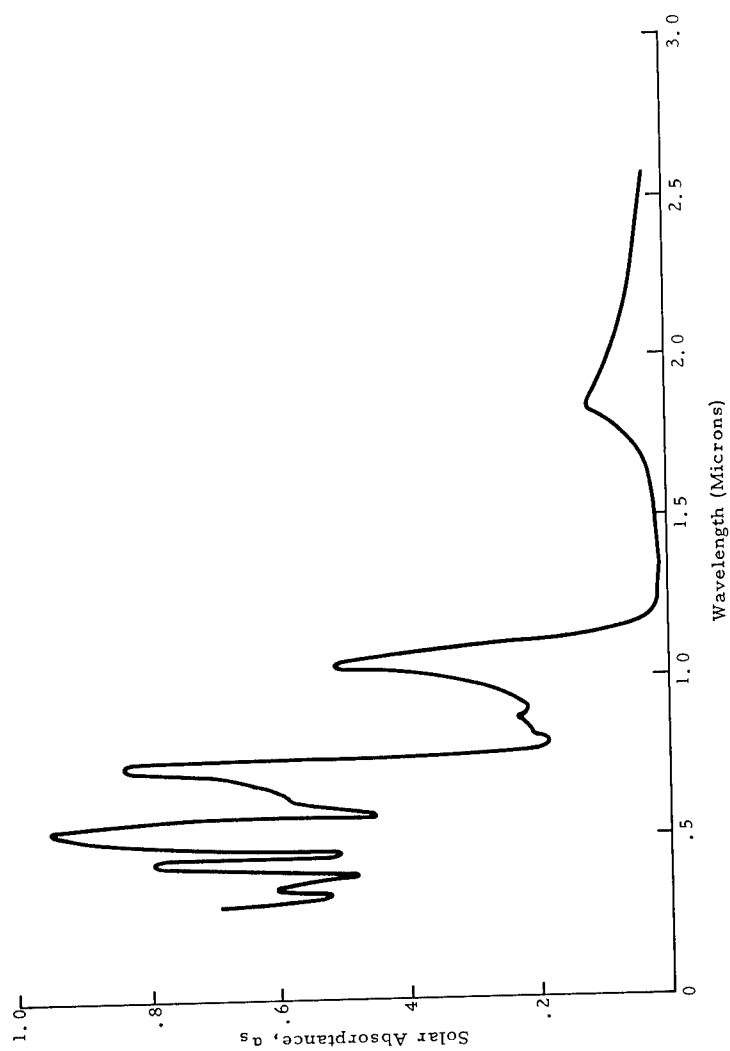
FIGURE 36.—Spectral dependence of solar absorptance.   (f) Surface 6, Al-SiO-Ge-SiO.
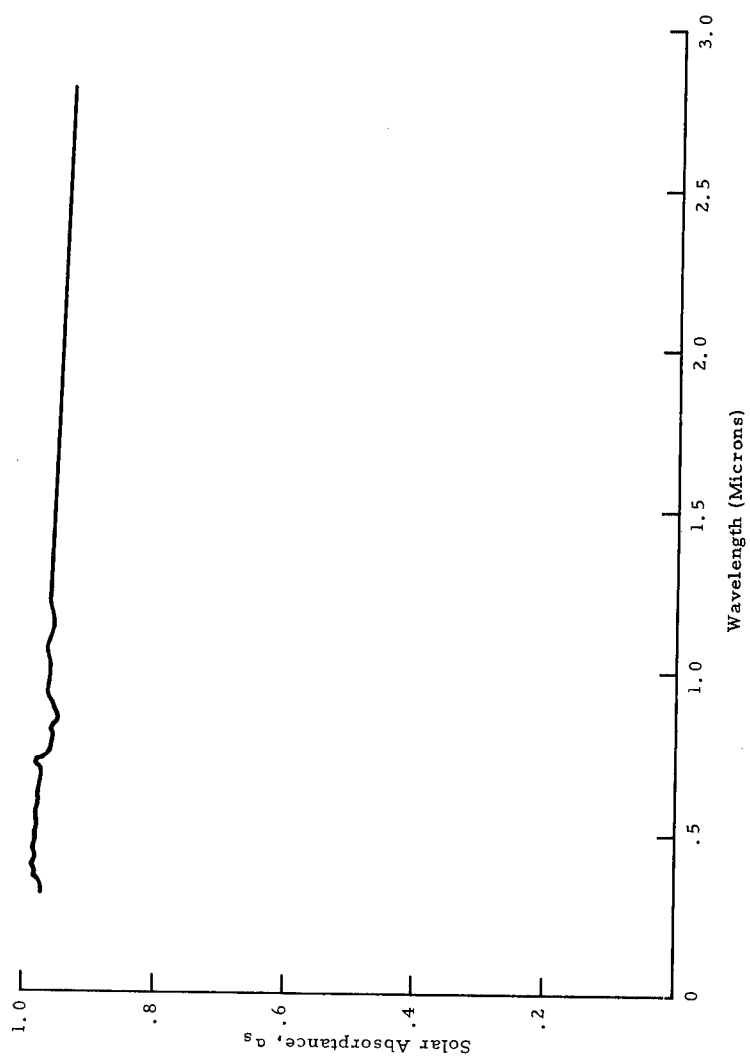
FIGURE 37.—Spectral dependence of solar absorptance.   (g) Surface 7, razor-blade reference.
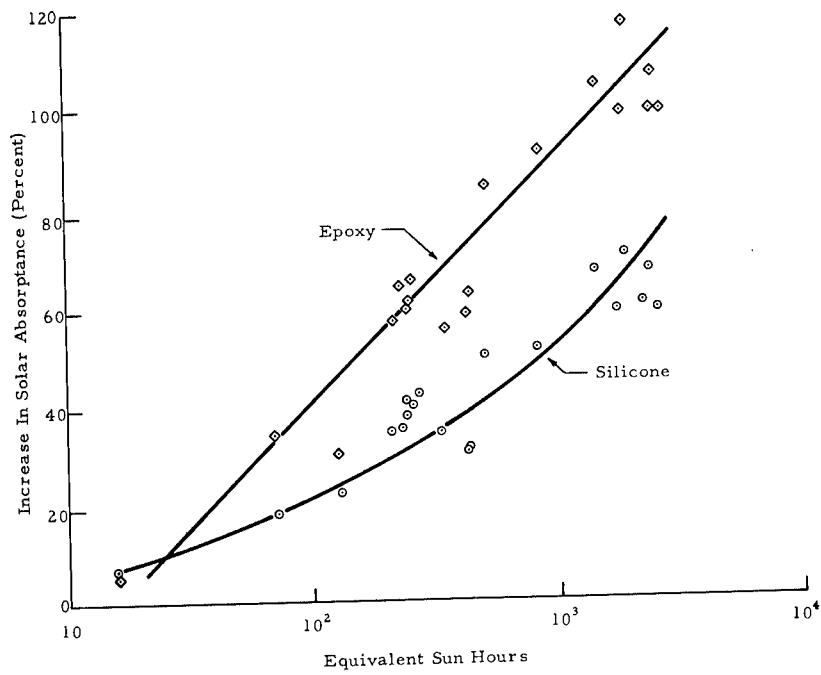
FIGURE 38.—Effect of exposure of test coatings to space environment.   (a) Surfaces 1 and 2.
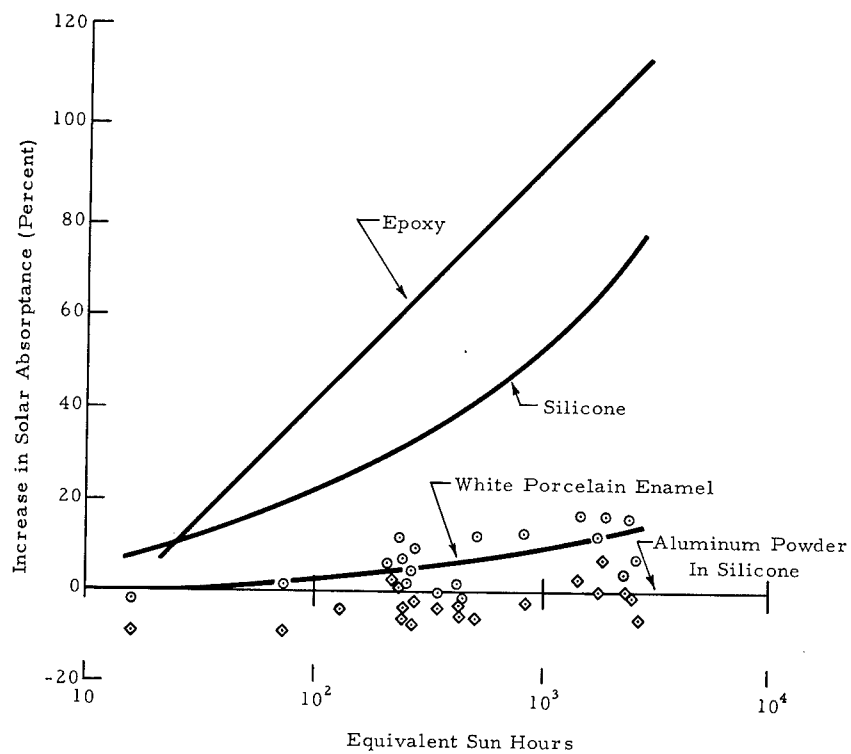
FIGURE 39.—Effect of exposure of test coatings to space environment.   (b) Surfaces
3 and 4.
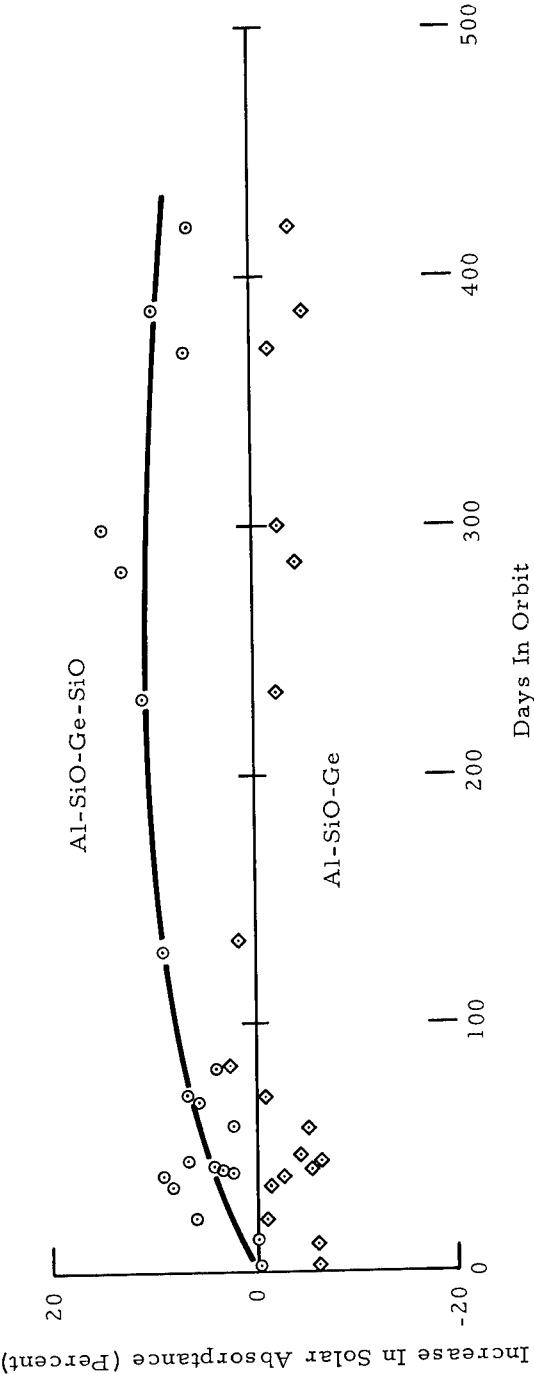
FIGURE 40.—Effect of exposure of test coatings to space environment.   (c) Surfaces 5 and 6.

Plastic Support

Test Surface on
1" dia . 016" Metal Disk

Mounting Cup

Thermistor for
Temperature Measurement

Polished Radiation
Shields
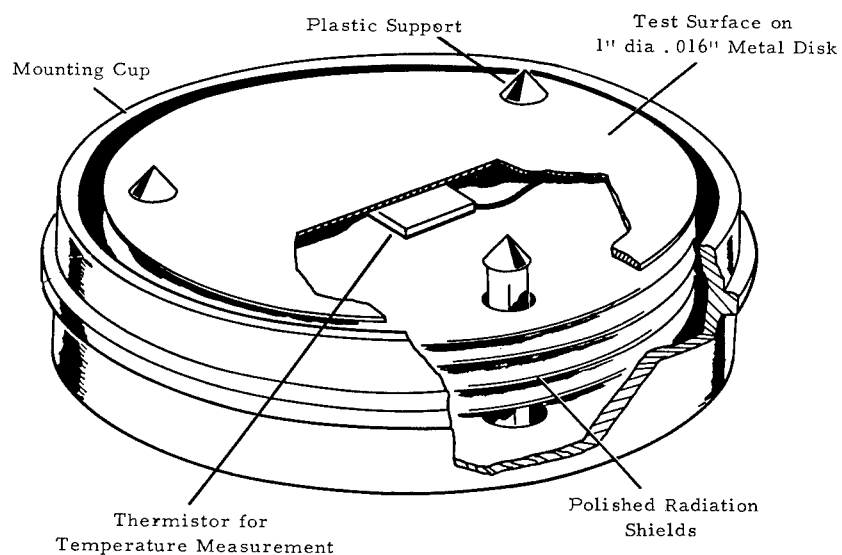
FIGURE 41.—Design of radiation sensors.

Razor-blade Edges
with Blackened Finish

1" Dia

Aluminum Base

Black-Body
Reference Surface

Grooved Surface

Front Plate 4" Dia 1/8" Alum

Thermistor on Base Plate

Base Plate 1/8" Alum

Six Test Surfaces
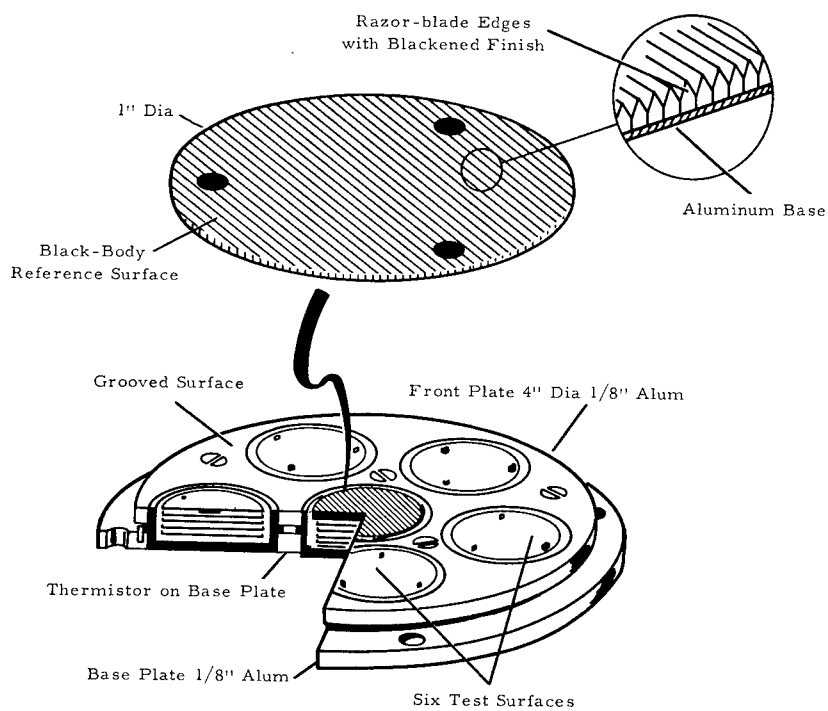
FIGURE 42.—Mounting of radiation sensors.
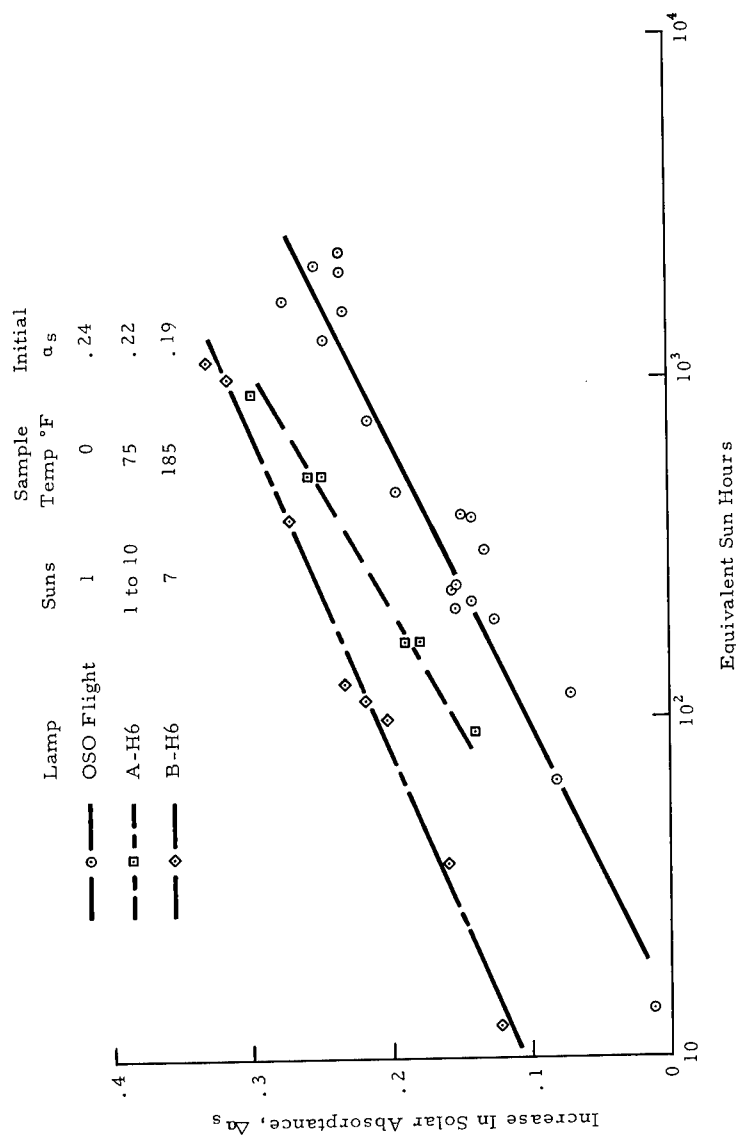
FIGURE 43.—Comparison of laboratory and flight degradation results.   (a) Surface 1, TiO₂ in epoxy.
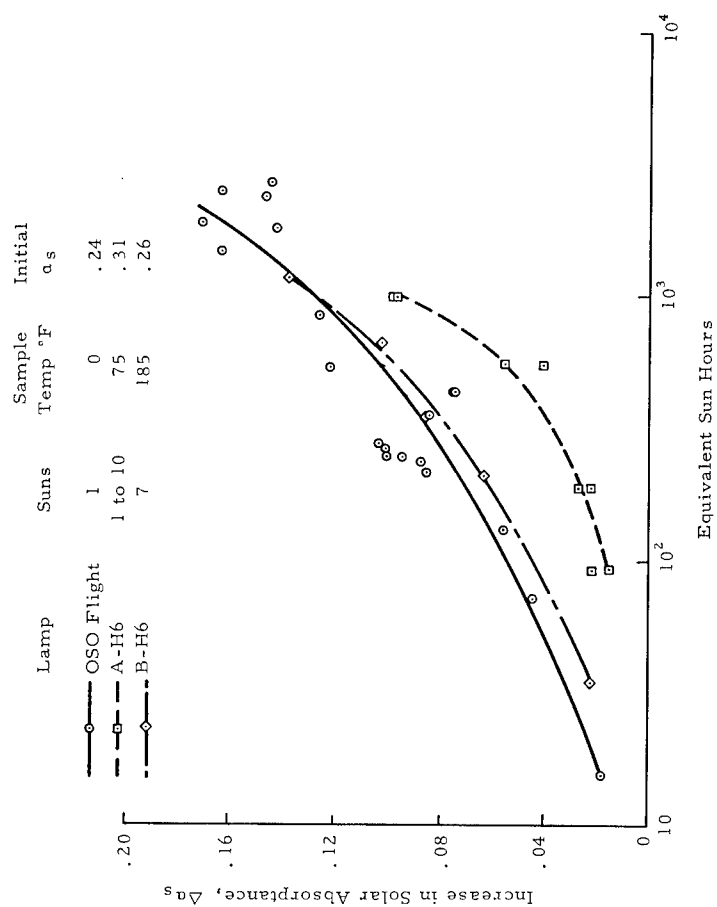
FIGURE 44.—Comparison of laboratory and flight degradation results. (b) Surface 2, TIO$_2$ in silicone

measurements in table 12. The percent increase in solar absorptance of test coatings No. 1 and No. 2 are shown in figure 38. The increase in solar-absorption of the epoxy coating was expected; however, the increase of the silicone-titania combination was unexpected. Figure 39 indicates the effect of space exposure on porcelain enamel and aluminum powder-in-silicone coatings (3) and (4), respectively. The alteration of solar absorptance for the layered coatings is given in figure 40. Interestingly enough, the thin germanium outer-coated sample shows no effect of erosion, while the silicon monoxide layer exhibits an increase in (α). The increase in the silicon monoxide-coated layer is probably due to the alteration of optical properties of the layer, rather than being an erosion effect. A comparison of the flight data with laboratory tests of the stability of coatings No. 1 and No. 2 are shown in figures 43 and 44.

Neel (ref. 27) presented the following general conclusions after analysis of measurements of the long-term stability of thermal radiation characteristics of several temperature control coatings during flight-in-space testing:

1. Exposure to the space environment increased the solar absorptance of several of the test coatings. The increase is presumed to be caused by ultraviolet radiation. The two white paints (TiO_2-in-epoxy and TiO_2-in-silicone) degraded rapidly, with the solar absorptance increasing in a period of 1,000 sun hours by nearly 100 percent for the epoxy paint, and approximately 50 percent for the silicone paint. The porcelain enamel was the most stable of the white coatings. Its absorptance increased less than 10 percent in 1,000 sun hours.

2. There was no evidence of deterioration of aluminum powder-in-silicone by nearly 3,000 sun hours of exposure.

3. No erosion of thin films of germanium, 110Å-thick, nor of silicon monoxide, 500Å thick, was evident. The measurements indicated an increase of about 10 percent in absorptance for the silicon monoxide film after about 200 days in orbit.

4. Comparisons of coating-degradation data obtained in laboratory ultraviolet-simulation equipment with the flight measurements illustrate the need for improving simulation techniques, and for obtaining a more fundamental understanding of the mechanism of ultraviolet degradation of thermal-control coatings.

Neel (ref. 26) has developed a second experiment for the S–17, Orbiting Solar Observatory. This device, which will measure the temperature response of twelve surfaces, is shown in figure 45. Two of these surfaces will be a razor-blade blackbody reference and a black paint for heat-flux measurements. Two white surfaces were used in continuation of a study correlating ultraviolet testing with flight data. Eight other coatings were tested for the project Apollo vehicle. A third flight experiment is

TABLE 12.—*Comparison of Laboratory and Flight Measurements of Thermal-Radiation Properties of Test Surfaces*

Surface	α_S/ϵ		ϵ		α_S		
					Laboratory		Flight
	Lab[a]	Flight	Lab	Flight	Normal	Average	
1. TiO$_2$ in epoxy	0.27	0.28	0.85	0.87	0.26	0.23	0.24
2. TiO$_2$ in silicone	.36	.32	.76	.76	.30	.27	.24
3. White porcelain enamel	.35	.32	.75	.75	.29	.26	.24
4. Aluminum powder in silicone	.96	.96	.26	.25	.23	.25	.24
5. Al-SiO-Ge	2.8	3.3	.13[b]	.11	.37	.36	.36
6. Al-SiO-Ge-SiO	2.5	2.8	.18[b]	.17	.47	.45	.47
7. Razor-blade reference	1.04	.98	.93	.96	.97	.97	.94

[a] Based on average values of α_S.
[b] Total normal emittance.
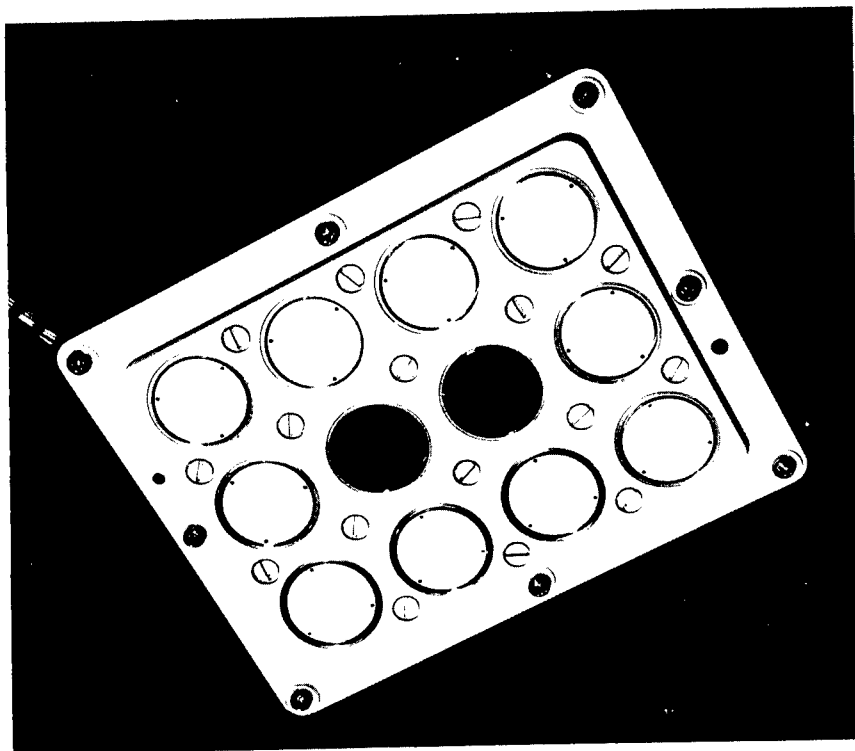
FIGURE 45.—Radiation sensor plate for S-17 orbiting solar observatory.

being planned on the OSO-S-57 satellite and further space experiments with temperature control coatings are required to meet anticipated needs of increasingly stable coatings for longer term exposures.

Parker, Neel, and Golub (ref. 28) obtained initial results indicating that polymers of vinyl chloride may be satisfactory as comparators in correlating the change in solar absorptance produced by exposure to ultraviolet irradiation in space and laboratory tests. Unfortunately, their experiment and other experiments were conducted in such a manner as to allow exposure of samples to the atmosphere between irradiation and measurement. While it is hazardous to generalize, the work of Farnsworth (ref. 16) showed markedly different results for samples which were allowed short contact times with the atmosphere. More carefully designed apparatus is required for measurements for ultraviolet degradation investigations.

ENERGY CONVERSION COATINGS

PHOTOVOLTAIC SOLAR CELLS

Conventional silicon solar cells convert solar thermal radiation into electrical energy, with a current efficiency of about 15 percent. However,

current solar cells are heavy and require rigid panels for support, which after launch fold out and lock into working position; a number of failures have been experienced with this arrangement. The ideal solar energy electrical conversion system would be a cell fabricated from a thin coating on a flexible plastic-film base. This type cell could be made in large extended sheets, folded away for launch, and unfolded in orbit.

H. E. Evans of the NASA Lewis Research Center is currently working on the development of semiconductor photovoltaic cells which can be applied and adhered to plastic substrates by sputtering. Such cells require six layers: (1) bottom silver electrode strip; (2) reactive indium-tin oxide transparent conduction layer; (3) photovoltaic layer; (4) reactive copper oxide layer; (5) top silver electrode strip; and, (6) final protective silicone coating. Various materials in the doped and undoped condition are being applied to substrates and tested with a highly automated apparatus. Materials tested by the sputtering process include gallium arsenide and cadmium sulfide. Present thin-film, photovoltaic cells convert about 3 percent of the solar energy into electrical energy. Investigations are designed to increase this efficiency.

EQUILIBRIUM TEMPERATURES OF IDEAL SPECTRALLY SELECTIVE SURFACES

Hibbard (ref. 29), NASA Lewis Research Center, developed an analytical model for obtaining the equilibrium temperatures of ideal spectrally-selective surfaces by which the monochromatic emissivity changed abruptly at a specific wavelength. These surfaces are fully described by the wavelength, λ, and by the departures Δ_1 and Δ_2 from total absorption or total reflection. In this analysis it was assumed that $\Delta = \Delta_1 = \Delta_2$. Where $\Delta > 0.5$, ϵ_λ is greater at short wavelengths than at long ones, and where $\Delta < 0.5$, ϵ_λ is greater at longer wavelengths. Where $\Delta = 0.5$, the surface is gray with an emissivity of 0.5. While this analytical model is not particularly advantageous for spacecraft temperature control, it is useful for energy-conversion calculations when high temperatures are required or for the calculation of cryogenic storage losses in space at low temperatures.

For a body exposed to unfocused radiation of normal incident solar flux equal to 1,350 w/m² when the blackbody distribution equals 5,800° K, and when all other sources of heat are disregarded, the radiant flux absorbed, $q(a)$ per m^2 of surface is:

$$q_{(a)} = 1{,}350 \left[\left(\frac{R_{s,\ o-\lambda}}{R_{s,\ o-oo}} \right) + \left(\frac{R_{s,\ \lambda-oo}}{R_{s,\ o-oo}} \right)^{(1-\Delta)} \right]$$

Where:

$\left(\dfrac{R_{s,\ o-\lambda}}{R_{s,\ o-oo}} \right)$ is the fraction of the total flux from the sun found at wavelengths shorter than (λ); and

$\left(\dfrac{R_{s,\ \lambda-oo}}{R_{s,\ o-oo}} \right)$ is the fraction at wavelengths longer than (λ).

The flux $q_{(r)}$ radiated away per unit area of surface is:

$$q_{(r)} = T^4 \left[\left(\frac{R_{T,\ o-\lambda}}{R_{T,\ o-oo}} \right) + \left(\frac{R_{T,\ \lambda-oo}}{R_{T,\ o-oo}} \right)^{(1-\Delta)} \right]$$

The temperatures for various surfaces perfectly insulated on the reverse side were calculated for various values of (λ) and are presented in figure
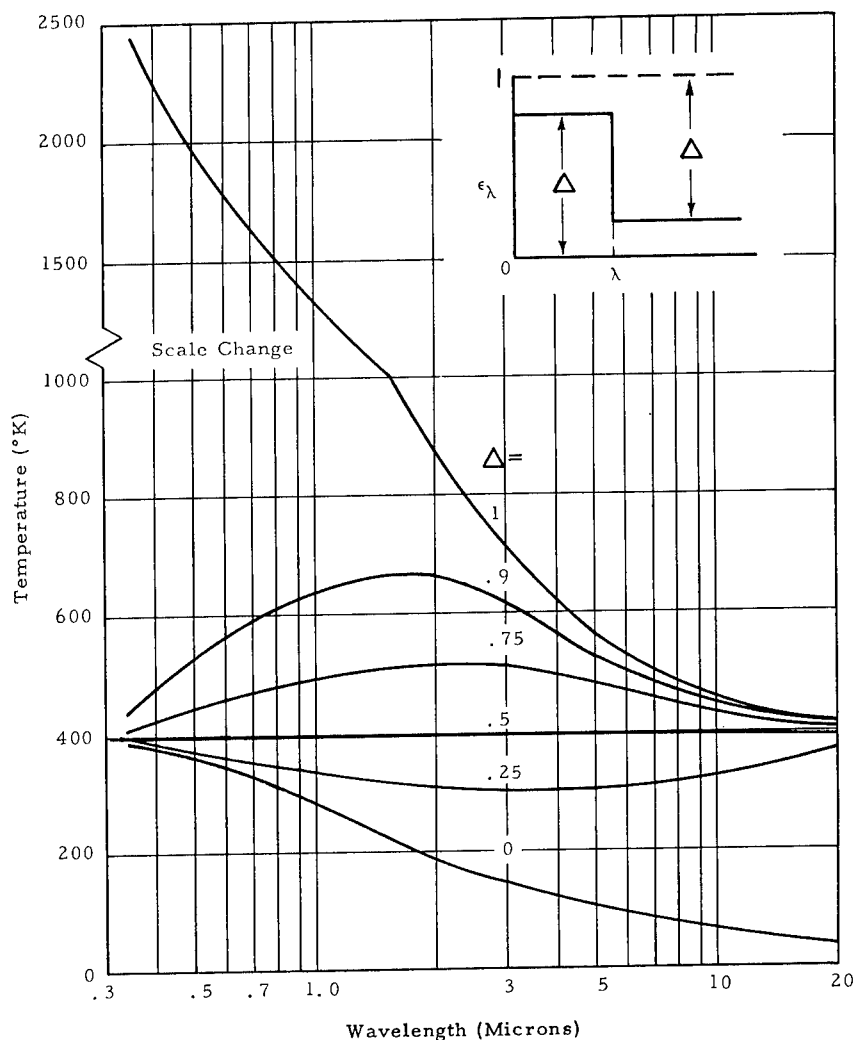
FIGURE 46.—Equilibrium temperatures of black insulated plate at earth's orbit as functions of Δ and λ.

46. Similar calculations were performed for concentration ratios of 100:1 and 10,000:1.

ANALYSIS OF SPECTRALLY SELECTIVE COLLECTOR SURFACES FOR APPLICATION WITH SOLAR-DRIVEN CARNOT SPACE-POWER SYSTEMS

Liebert and Hibbard (ref. 30), NASA Lewis Research Center, published a theoretical analysis of solar-driven Carnot space-power systems utilizing spectrally selective collector surfaces. Prior analysis by Shaffer (ref. 31) used only the limiting values of a step change from unity to zero absorptance. Liebert and Hibbard used the analytical model of Hibbard (discussed above) for calculating the energy available to drive a Carnot-cycle engine. The energy received (W_1) from a solar flux concentrator, less the reflected energy (W_2) and the reradiated energy (W_3), is the energy available to drive the Carnot engine.

$$W_1 - W_2 = 0.135C \left[\left(\frac{R_{o-\lambda}}{R_{o-oo}} \right)_{5,800\,K} \Delta + \left(\frac{R_{\lambda-oo}}{R_{o-oo}} \right)_{5,800\,K}^{(1-\Delta)} \right]$$

where (C) is the ratio of the concentrator area to that of the collector, $(R_{o-\lambda})/(R_{o-oo})$ is the ratio of energy found with wavelengths shorter than the wavelength (λ) of the step function, and $(R_{\lambda-oo}/R_{o-oo})$ is the fraction longer than (λ). The flux radiated by the collector surface at a temperature (T_1) is equal to

$$W_3 = \sigma T_1^4 \left[\left(\frac{R_{o-\lambda}}{R_{o-oo}} \right)_{T_1} \Delta + \left(\frac{R_{\lambda-oo}}{R_{o-oo}} \right)_{T_1}^{(1-\Delta)} \right]$$

The flux (W_4) available to the Carnot cycle is equal to $W_1 - W_2 - W_3$, and the engine temperature is (T_2). Therefore, the flux converted to work (W_5) is simply:

$$\left(\frac{T_1 - T_2}{T_1} \right) W_4$$

The rejected flux is:

$$\left[1 - \left(\frac{T_1 - T_2}{T_1} \right) \right] W_4 \quad \text{or} \quad \left(\frac{T_2}{T_1} \right) W_4$$

The radiated flux at equilibrium is:

$$A\alpha T_2^4 = \left(\frac{T_2}{T_1} \right) W_4$$

The temperature of the radiator is:

$$T_2 = \left(\frac{W_4}{A\alpha T_1} \right)^{1/3}$$

(A) is the ratio of radiator to collector areas. The Carnot powers and efficiency can now be collected for chosen values of T_1, C, A, λ, and Δ, as well as the overall cycle efficiency ($W_5/0.135C$).

The results presented graphically in figures 47 and 48 are very interesting and useful in the design of selective surfaces for solar-driven Carnot engines. The maximum overall cycle efficiency of 55 percent is obtained when $\Delta = 1.0$, $\lambda = 1.22$, with a power output of 0.074 w/cm^2. For less selective surfaces, the efficiency drops very rapidly. The effect of increasing the concentrator-to-collector area results in a rapidly decreasing advantage for spectrally selective surfaces as compared to black surfaces. For instance, at $C = 100$ the ideal surface yields 0.090 w/cm^2 as compared with 0.074 w/cm^2 for unfocused radiation, and is only 22 percent greater than the 0.071 w/cm^2 obtained with a black collector. When $C = 10,000$, the advantages of a selective surface are negligible. Although efficiencies for focused radiation equal to the unfocused case are obtained when the radiator area is greater than the collector area, such an area ratio may be unsuitable in space vehicle design. The use of selective surfaces can create practical design problems because of excessive temperatures. If $\Delta = 0.9$, $\lambda = 1.0$, and $C = 100$ the power output is 0.065 w/cm^2 which is substantially the same power obtained from a 0.9 gray surface at the same concentration ratio. However, the selective surface yields a driving temperature of 1,100° K and a sink temperature of 237° K; whereas the gray surface equivalent temperatures are 810° K and 279° K. This is a significant difference from an engineering-design standpoint.

This analysis provides guidelines not previously available for several coating design parameters.

HIGH EMITTANCE SURFACES

Slemp (ref. 32) has investigated the effect of surface treatment and pre-oxidation on the spectral and total-normal emittance of Inconel, Inconel X, and type 347 stainless steel. Measurements of emittance were made at 900, 1,200, 1,500, and 1,800° F. Surface characterizations were: (1) "as received" (AR); (2) etched in two different acid solutions (E_1) and (E_2); (3) grit-blasted with −100 and 40–60 silicon carbide grit (CB_1) and (CB_2); and (4) polished (240, 320, 400, and 600 grit papers) (P). All specimens were oxidized in a clean electric furnace preheated to the desired temperature. Inconel and Inconel X were oxidized for 20 min. at 2,000° F; type 347 stainless steel for 20 min at 1,800° F. Grit-blasted (GB_2) Inconel was oxidized for 20 min, 2, 4, and 8 hr at 2,000° F. Emittance measurements were made in apparatus developed by Slemp (ref. 33).

Surfaces of Inconel, Inconel X, and 347 stainless steel were obtained which exhibited stable spectral emittances in excess of 0.90 over the wavelength interval 1 to 15μ. Surfaces of oxidized Inconel, Inconel X, and 347 stainless steel yielded stable total emittances of 0.97, 0.92, and 0.91, respectively. Because all measurements were made in air, the vacuum stability of these potential space-radiator surfaces is unknown.
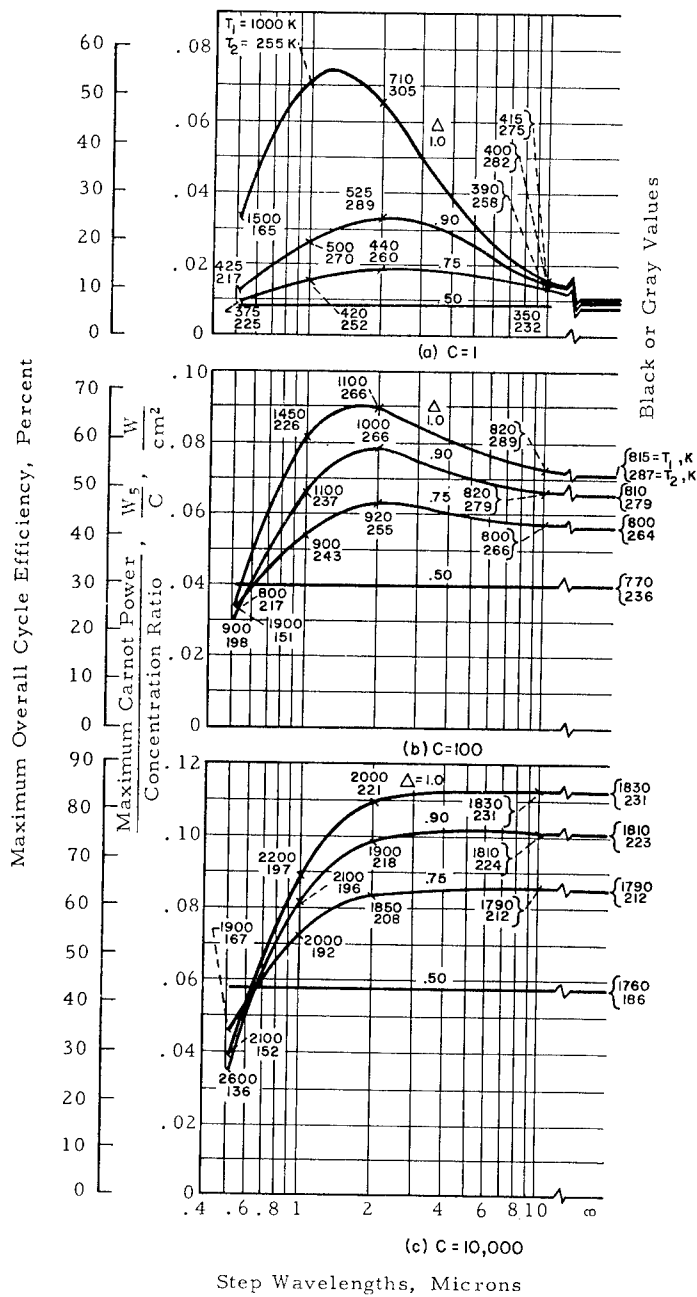
FIGURE 47.—Variation of maximum Carnot work and over-all efficiency with cutoff wavelength and Δ as parameter for C = A.
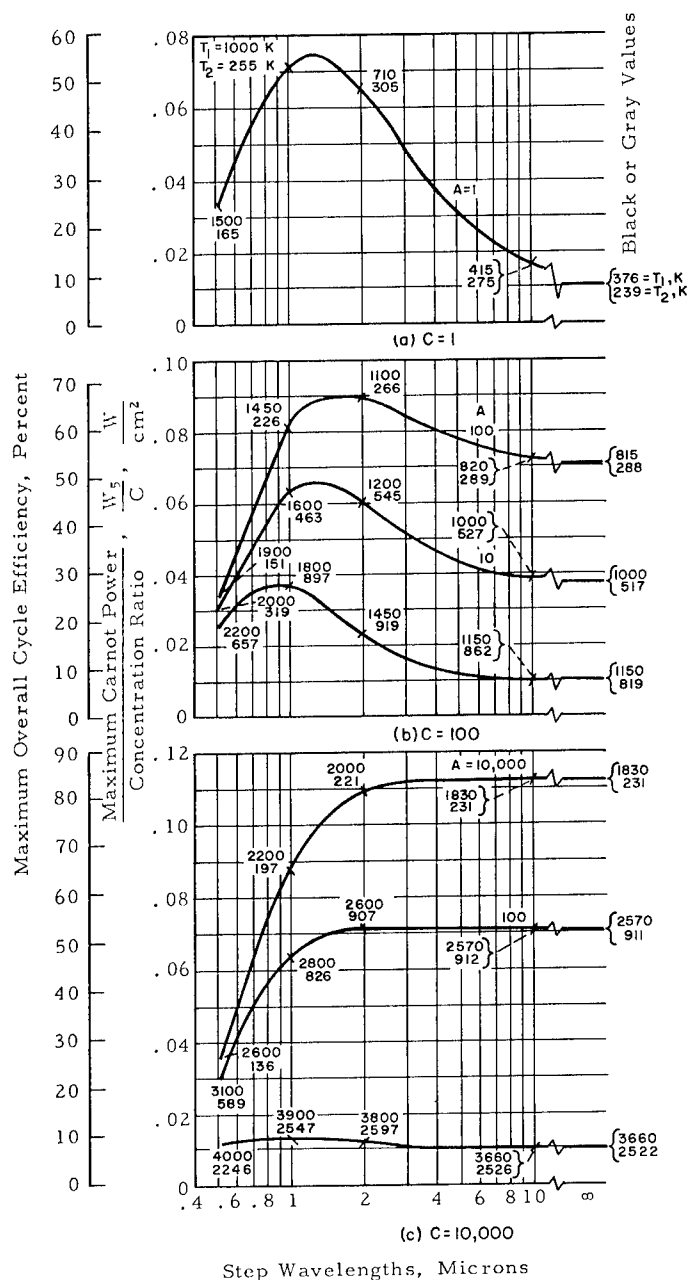
FIGURE 48.—Variation of the maximum Carnot work and over-all efficiency with cutoff wavelength and A as parameter for Δ = 1.

However, they appear to have a future use in some applications. (See table 15.)

Wade and Slemp (ref. 34), NASA Langley Research Center, published additional total emittance data for refractory materials useful as high-temperature radiators or dissipators. (See tables 13 and 14.) The Inconel surface was saturated with sodium dichromate to give a stable, adherent, oxide film. Samples held at 1,800° F for 30 min showed a definite decrease in emittance. X-ray diffraction of the sample after the decrease in emittance, showed the presence of NiO and Cr_2O_3.

Angular measurements of emitted energy showed only small deviations from Lambert's cosine law for angles up to 50° from normal to the surface.

Stably-oxidized, aluminum oxide paint was sprayed on Inconel strips in thicknesses of 1, 2, and 3 mils. The measured emittances were 0.82 at 600° F and 0.83 at 1,800° F for all three coatings.

The cermet materials listed in table 16 are produced by the Haynes Satellite Company, and consist primarily of chromium-aluminum composites.

Walker and Casey (ref. 35), NASA Langley Research Center, recently presented data for the total normal emittance from 1,200° F to 1,900° F and for normal spectral emittance data at 1,400° R. The results show that for an 0.253-inch-thick specimen of boron nitride, $\epsilon_t = 0.79$ at 1,210° F and increases approximately linearly with temperature up to 0.81 at 1,860° F. Normal spectral emittance data obtained from the same thickness specimen over the wavelength range 0.5 to 15μ showed an increase from 0.16 at 0.7_λ to 0.30 at 2.0_λ, 0.9 at 3.5_λ, and 0.95 at 6.0_λ. A reflection band reduced the emittance to 0.64 at 6.8_λ, but the emittance rose back to 0.85 at 8.0_λ and stayed near 0.90 out to 15.0_λ except for a small minimum at 13.0_λ.

These results show that in spite of the apparent white color indicating low visible-emittance, boron nitride must be considered as a candidate material for high-temperature applications subjected to aerodynamic-heating. The application of boron nitride will be restricted in many cases by its poor oxidation resistance.

Wade and Casey (ref. 36), NASA Langley Research Center, measured the total hemispherical-emittance of several nickel-titanium cemented-carbides over the temperature range 600° F to 1,600° F. Kennametal Corporation specimens having stably-oxidized-"as received" surfaces had values of $(\epsilon) = 0.90$ to 0.94 at 600° F and 0.88 to 0.92 at 1,600° F. Specimens polished prior to oxidation possessed values of 0.82 to 0.89 at 600° F and from 0.85 to 0.87 at 1,600° F.

Wade (ref. 37) previously measured the emittance of high-temperature, oxidizer metals at elevated temperatures.

TABLE 13.—*Oxidized Inconel*

Specimen (*)	Preoxidation treatment (*)	Total normal emittance at temperature, °F				Other surface properties
		900	1,200	1,500	1,800	
ARO_1	AR	0.64	0.68	0.76	0.80	Fairly adherent, reproducible, gray with small green blotches.
E_1O_1	E_1	.69	.71	.77	.81	Very adherent, highly reproducible, gray-black.
PO_1	P	.64	.70	.76	.79	Fairly adherent, not very reproducible, green-gray.
GB_2O_1	GB_2	.77	.80	.85	.87	Not very adherent or reproducible, gray-green.
$GB_2E_1O_1$	GB_2 followed by E_1	.72	.74	.79	.81	Rough, very adherent, highly reproducible, gray-black.
$GB_1E_1O_1$	GB_1 followed by E_1	.68	.72	.78	.80	Smooth, very adherent, highly reproducible, gray-black.
GB_2O_3	GB_2	.86	.94	.96	.97	Adherent, reproducible, more green than the GB_2O_1.
GB_2O_4	GB_2	.88	.94	.96	.97	Adherent, reproducible, stable. The green color has disappeared leaving a gray-black oxide.
GB_2O_5	GB_2	.87	.94	.96	.97	Very similar to GB_2O_4.

TABLE 14.—*Oxidized Inconel-X*

Specimen (*)	Preoxidation treatment (*)	Total normal emittance at temperature, °F				Other surface properties
		900	1,200	1,500	1,800	
ARO_1	AR	0.82	0.84	0.86	0.88	Adherent, uniform, reproducible, gray-black.
E_1O_1	E_1	.80	.82	.84	.87	Very smooth, adherent, uniform, reproducible, gray-black.
PO_1	P	.80	.82	.86	.89	Not very reproducible, light gray blotches.
GB_2O_1	GB_2	.85	.88	.90	.92	Rough, adherent, reproducible, slightly blotched gray-black.
$GB_1R_1O_1$	GB_1 followed by E_1	.85	.88	.89	.91	Very uniform, adherent, reproducible, gray-black.
$GB_2E_1O_1$	GB_2 followed by E_1	.86	.88	.90	.92	Very uniform, adherent, reproducible, gray-black.

TABLE 15.—*Oxidized Stainless Steel Type 347*

Specimen (*)	Preoxidation treatment (*)	Total normal emittance at temperature, °F				Other surface properties
		900	1,200	1,500	1,800	
ARO_2	AR	0.82	0.86	0.89	0.91	Not very reproducible, nonuniform, blotched light gray.
E_2O_2	E_2	.84	.87	.90	.91	Rough, uniform, adherent, reproducible, gray-black.
PO_2	P	.74	.77	.81	.83	Very smooth, uniform, adherent, reproducible, gray-black.
GB_2O_2	GB_2	.85	.88	.90	.92	Not reproducible, nonuniform, blotched.
$GB_1E_2O_2$	GB_1 followed by E_2	.81	.83	.86	.88	Smoother than E_2O_2, uniform, adherent, reproducible, gray-black.
$GB_2E_2O_2$	GB_2 followed by E_2	.84	.86	.88	.90	Rougher than E_2O_2, uniform, reproducible, adherence not as good as $GB_1E_2O_2$, gray-black.

TABLE 16.—*Total Normal-Emittance of Ceramics and Cermets*

	600° F	800° F	1,600° F	1,800° F
Ceramics				
Norton Crystolon-R	0.90	------	------	0.84
Alfred U. SiC+C	.90	------	------	.70
Nat. Crucible SiC+C	.94	------	------	.75
Carborundum SiC+Si	.94	------	------	.62
Carborundum Si₃N₄	.89	------	------	.78
Cermets				
LT-1 (stably-oxidized)	.79	------	0.90	------
LT-1 (flame-sprayed)	------	0.84	------	.90
LT-1B (stably-oxidized)	.79	------	.94	------
LT-1B (flame-sprayed)	------	.88	------	.94
LT-2 (stably-oxidized)	.76	------	.91	------
LT-2 (flame-sprayed)	------	.86	------	.90

Gruer (ref. 38) of McDonnell Aircraft Corporation, working under NASA contract, developed a process for obtaining total-emittances greater than 0.8 at 1,800° F for René 41 and L–605 alloys. Steps in the sample preparations were as follows:

René 41 Alloy
1. Oxidize at 1,950° F for ½ hr in an air-atmosphere furnace.
2. Remove from furnace and cool in air.
3. Heat at 1,400° F for 16 hr in an air-atmosphere furnace. This step provides the required aging and oxidation characteristics.
4. Remove from furnace and cool in air.

L–605 Alloy
1. Oxidize at 1,950° F for ½ hr in an atmosphere furnace.
2. Remove from furnace and cool in air.

The oxide finish is tightly adherent and is capable of being flexed without flaking or peeling from the base metal. It also provides an oxidation-and-corrosion-resistant surface having very good thermal shock resistance.

ANALYSIS OF THERMAL PROTECTION OF CRYOGENIC STORAGE IN SPACE VEHICLES

Smolak, Knoll, and Wallner (ref. 39), in making an extensive analysis of the liquid hydrogen losses from space vehicle storage tanks, postulated a reasonable rocket configuration when using various types of thicknesses of insulations. The result of the analysis showed that the loss of liquid hydrogen could be kept sufficiently low so that a manned mission to Mars might be feasible. However, only gray external surfaces having $\alpha/\epsilon = 1.0$ were considered.

More recently, Liebert and Hibbard (ref. 40) performed an analysis to determine the effectiveness of solar reflectors in reducing heat transfer through the insulation of cryogenic-fuel tanks located in deep space.

They considered the effect of surface coatings with ratios of absorptance to emittance varying from 0.1 to 1.0 when applied to the external surfaces of bulk insulation or multifoil insulation. Calculations of this type, by pointing out specific requirements, provide clear guidelines on the need for developing materials with lower (α/ϵ) ratios. An (α/ϵ) ratio of 0.2 reduces the heat-leak to about 60 percent that of an (α/ϵ) of 1.0 in the case of a bulk insulation, and to about 20 percent the leak-through for a multifoil system.

COMMERCIAL IMPLICATIONS

TEMPERATURE CONTROL COATINGS

The general concepts and importance of thermal control as developed for space applications are of much less importance to terrestrial uses since the presence of the atmosphere imposes a major direct influence on most inhabited buildings. However, incremental improvement in residential temperature control can certainly be affected. The effects of thermal control coatings are more important in limiting the summer cooling load than in decreasing the winter heating requirements because of the higher energy cost of cooling incident to larger solar inputs in those lower latitudes requiring air conditioning.

The application of temperature control paints, having a low solar absorptance (α), to storage tanks and vessels containing volatile fluids is currently a minor practice in the petroleum industry. The use of aluminum-pigmented paints for temperature control purposes will be encouraged partly because of the results obtained by the space program on temperature control surfaces.

Even more important than space temperature control concepts will be the possibility of new coating materials or a better understanding of older coatings. It is interesting to observe the evolution in the last six years of space temperature control coatings. The first small weight restricted satellites (Vanguard II, Explorer I) were coated with complicated vacuum-deposited or flame-sprayed coatings. Because the more recent space vehicles are larger they are less sensitive to weight restrictions, and as a result the large Echo satellites used a commercial-conversion aluminum phosphate coating. In general, the requirements for space applications are moving closer to the general commercial technology.

The major technological transfers will probably come from the current work in identifying the mechanism of photolysis in coatings. In general, photodegradation of coatings affects the organic vehicle more than it does the inorganic pigment. However, complex interaction effects between vehicle and pigments are possible. Clarification of this kind of phenomenon will contribute to coating technology and eventually result in better paints. This does not imply that the mechanisms of photodegradation in vacuum and in space are identical. Currently, it is

assumed that in the atmosphere, once polymer chains are broken, oxygen is present to react with the hydrocarbons, while in space where oxygen is not present cross linkage of the polymers occurs. Elucidation of the mechanisms of degradation in vacuum may provide insight into the atmospheric-reaction degradation, even though the mechanisms are different.

ENERGY CONVERSION COATINGS

The development of large-sheet, photovoltaic-conversion cells for application in space will certainly demonstrate the technical feasibility of this concept for commercial applications. However, the economic evaluation of these cells can only follow after the technical feasibility is demonstrated. This event appears to be at least two to five years in the future, based on the current rate of progress.

In evaluating the technological implications of energy conversion, the solar energy utilization field requires the most careful consideration. Available literature indicates the level of sophistication of the analysis in this field along with the dearth of synthesis of the data. The various design factors, such as collector angle, optimum optical properties for the collector, and the relative trade-offs between collector, storage, and auxiliary power required for residential and commercial heating, have been carefully analyzed. The utilization of solar energy heating presently does not depend upon additional decimal points coming from more and more exact analysis, but from the equivalent of an Edison who can creatively synthesize the present analysis with the required technology.

Kastens (ref. 41), clearly stated the economic analysis problems associated with solar heating. At present, 75 percent of the cost of a residential solar heating system is accounted for by collectors that cost $2 to $3 per sq ft. Solar heating would be economically feasible at $1 per sq ft of collector, and probably quite attractive at prices of $.50 per sq ft. While numerous and substantial efforts are being made in the development of solar collectors they are still complicated and intricate devices requiring large amounts of skilled handwork. Completely new approaches will be required to reduce the costs to the required levels.

Kastens also points out that the alternative of increasing the collector efficiency is a cost-reduction approach. If collector efficiency increases by 10 percent, then the cost is reduced accordingly. NASA in developing selective energy-absorbing surfaces, for which data is not currently available, believes that increases in efficiency of solar collectors for heating are likely to be of the order of 20 to 50 percent rather than the required factor of 10. Selective surfaces have limited use in those air conditioning systems using the collector as an emitter for heat sink purposes.

A review of the NASA contributions to temperature control and energy conversion, shows that the concepts and techniques required to build the

Echo I and II satellites are useful in developing economically-attractive solar collectors. The fabrication and coating of large, plastic, inflatable structures offers attractive possibilities for solar collectors. Plastic film is inexpensive, and can be produced in multiple layers of large sheets. The design of a water or air-transfer-media coated plastic collector, which could be unrolled and attached to existing roofs with adhesives for relatively low cost, appears feasible. Obviously a considerable amount of design work is required to bring this concept to fruition.

Solid Lubrication Coatings

The space programs require light and reliable bearings, seals, and heavily-loaded movable joints. As more complex and larger space vehicles are launched, the use of mechanical devices will increase. Conventional hydrocarbon lubricants possess vapor pressures that prohibit their use for extended periods of time except in sealed systems. In the atmosphere, some degree of lubrication is derived from the oxide films normally present on metal surfaces; when a lubricant film is worn away, ruptured, or decomposed, the metal is oxidized by the atmosphere and some degree of surface protection is restored. However, in the vacuum of space, oxide surfaces are not renewed. After oxide-surface films and absorbed gases are cleaned from a surface, the metal surfaces "vacuum weld" by interdiffusion. Thus, coefficients of friction increase to levels requiring the shear strength of relatively large structural members in machine design.

Another complicating factor in bearing design is the absence of a gas phase to assist in dissipating the heat generated at the contacting or sliding surfaces. If liquids are present they are not the usual well-behaved liquids, such as water or organics, but more commonly cryogenic fluids (liquid N_2, H_2 or O_2) or liquid heat-transfer media such as liquid sodium or alkali metal alloys. NASA and its predecessor, NACA, have long been responsible for developing lubrication systems for extreme environments. These problems will continue as increasing loads, greater service life, reliability, higher (and lower) service temperatures, and decreased weight are constant objectives. As one set of objectives are met, newer requirements will take their place.

COATINGS FOR LUBRICATION IN THE SPACE ENVIRONMENT

The process of wear of bearing surfaces is principally an equilibrium process between the formation and destruction or removal of a coherent oxide film from metal surfaces. In space, the low pressure precludes the presence of oxygen and after oxide films are removed clean surfaces are produced. The bonding by adhesion and interdiffusion of metal surfaces is not well understood except to the extent that such surfaces possess

extremely high coefficients of friction.   The energy required to overcome these frictional loads is not known to be available on space missions.

Excellent reviews of the complex problems associated with wear and lubrication of surfaces in space have been given by Johnson (ref. 1), NASA Lewis Research Center, Kingsbury and McKannan (ref. 2), NASA Marshall Space Flight Center, Jaffe and Rittenhouse NASA Jet Propulsion Laboratory (ref. 3), and Lad (ref. 4), NASA Lewis Research Center.   Clauss, O'Hara, and Cooke (ref. 5), give a complete survey of the vacuum lubrication problems and engineering solutions available up to the end of 1961.   Useful dry-film lubricants include molybdenum disulphide applied with various binders, metal films of silver or deposited barium, or certain cobalt-base-bearing alloys.   The cobalt alloys are not true coated systems, but contain sufficient oxide inclusions to replace disrupted oxide films.   Unfortunately, vacuum testing is so expensive in ultrahigh-vacuum systems that statistically reliable design data is not yet available, though the general situation is probably correctly understood.   Friction and wear data are unreliable when obtained from a vacuum system whose pressure is greater than 10^{-6} Torr.   And at lower pressures, extreme care must be exercised, or backstreaming from oil diffusion and force pumps may render the data useless.   It is not entirely clear how backstreaming can be completely eliminated even though pump manufacturers insist that the problem may be overcome.

SLIDING FRICTION

Buckley and Johnson (ref. 6), NASA Lewis Research Center, investigated friction, wear, decomposition, and evaporation rates of various polymers with and without inorganic fillers incorporated into their structure.   Hemispherical-rider specimens with a $3/16$-inch radius and under a 1-kg load were applied against flat disk surfaces.   Sliding velocities from 30 to 1,480 ft/min were investigated in a 10^{-9} Torr vacuum.   A mass spectrometer was used to identify the polymer decomposition products.   The results indicated that under the conditions tested, the polyimide-polymer compositions had relatively good friction-and-wear properties in a 10^{-9} Torr vacuum.   Results for polytetrafluorethylene ("Teflon" PTFE) indicate that copper powder and glass fillers markedly reduced the rate of wear, while added MoS_2 offered no further improvement in frictional properties.   The results are significant for the design of low-load, high-speed, sliding-friction bearings and seals. Buckley and Johnson (ref. 7) determined the evaporation rates of several solid lubricants in a 10^{-8} Torr vacuum at temperatures of 55° to 1,100° F.

Buckley and Johnson (ref. 8) investigated the friction, wear, and welding characteristics of nickel-oxygen, nickel-tin and iron-sulfur alloys. Test specimens were $3/16$-inch radius hemispherical-riders sliding under a

1-kg load against rotating disks at a velocity of 28 to 1,800 feet per minute at 75° F. The results indicate that 1.35 to 7.5 percent nickel oxide contained in electrolytic nickel resulted in friction and wear properties in vacuum equal to that obtained for nickel-base alloys in the atmosphere (760 mm Hg air). Additions of 20 percent tin to electrolytic nickel reduced friction and wear by a factor of 10. The presence of 0.10–0.45 percent sulfur, as ferrous sulfide, in electrolytic iron, reduced friction-wear-and-welding of electrolytic iron at low ambient pressures. Nickel oxide serves to prevent metal-to-metal welding as a lubrication layer while the tin alloy of nickel (Ni_3Sn), due to its low melting point, is softened and smeared over the nickel surfaces.

Thin-film lubrication by gallium has been conceived and investigated by Buckley and Johnson (ref. 9). Gallium melts at 86° F and tends to form alloys or solutions with many metals. It possesses good wetting, low vapor pressure, and high thermal conductivity properties, all of which recommend gallium as a sliding-friction bearing. Interestingly enough, gallium has markedly better friction and wear properties in vacuum than in air. Also it has better lubrication properties at high speeds than low speeds. The exact reasons for its behavior are not clear. Since gallium tends to diffuse into metal surfaces at high temperatures, its lubricating properties are time dependent. However, with the development of suitable matrix materials, gallium appears to offer excellent potentials for further development.

Demorest and McKannan (ref. 10), NASA Marshall Space Flight Center, investigated twelve different systems of molybdenum disulfide and binders, mixtures of gold, MoS_2 in sodium silicate, and burnished MoS_2 on a flame-sprayed coating of zirconium silicate for use in slowly oscillating journal bearings loaded from 15,000 to 25,000 psi over a temperature range $-100°$ C to $+200°$ C at 10^{-6} Torr vacuum. Typical coefficients of friction were 0.1.

Hopkins and Gaddis (ref. 11) at the Midwest Research Institute, working under NASA contract NAS 8–1540 for Marshall Space Flight Center, are investigating the use of various inorganic coatings for vacuum lubrication. One hundred and sixty-five materials were screened on the basis of physical and chemical properties. Twenty-two of these materials were tested. Nine materials, BiI_3, Bi_2Te_3, $CdBr_2$-$4H_2O$, $AuTe_2$, $MoSe_2$, $AgBrO_3$, $AgCl$, WS_2, and WSe_2 exhibited friction coefficients of 0.22 or less. These materials will be incorporated into solid-lubricant films for further screening. Binders were formulated from potassium silicate (Kasil 88) plus additions of sodium phosphate, potassium phosphate, sodium borate, or sodium fluoride. One admixture of each type was used in varying amounts. Several methods of applying and curing

binders were investigated, though no large differences were noted. No outstanding binder has been developed.

MOLYBDENUM DISULFIDE LUBRICANTS

Johnson, Godfrey, and Bisson (ref. 12) conducted an experimental investigation into the mechanism of friction, lubrication, and wear of surfaces in sliding contact at ambient temperature. The sliding velocities tested varied from 50 to 8,000 ft/min with loads from 169 to 1,543 g, which resulted in initial Hertz-surface stresses of 108,000 to 225,000 psi. These experiments clearly indicated the effective nature of molybdenum disulfide for the lubrication of heavily-loaded journal bearings. Low coefficients of friction, chemical and thermal stability, and the adhesion to metal surfaces were all determined to contribute to the excellent lubrication properties of MoS_2.

Later Godfrey and Nelson (ref. 13) conducted related experiments at temperatures up to 1,050° F. The rate of oxidation of MoS_2 was determined up to 1,100° F. The rate of oxidation is slight up to 750° F, but above this temperature it increases very rapidly. The oxidation product is MoO_3, which produces a high frictional coefficient by itself. It was determined that MoS_2 maintains its original hexagonal structure when heated to 1,000° F in vacuum. These experiments were extremely useful in establishing the ambient and high-temperature lubrication properties of molybdenum disulfide.

One of the problems concerning the development of molybdenum disulfide as a solid-coating lubricant was the development of material systems suitable for retaining MoS_2 for extended periods of time. Johnson, Swikert, Bisson, and Edmond (ref. 14), NASA Lewis Research Center, developed and studied the friction and wear of hot pressed bearing materials. Mixtures of up to 35 percent MoS_2, silver, and 5 percent copper were hot pressed and tested in sliding-friction experiments. It was established that 10 percent MoS_2 additions provided both the minimum coefficient of friction and the lowest wear rate. The lubrication properties were developed by a film of MoS_2 between the surfaces. Additions of MoS_2 less than 10 percent resulted in higher wear; and additions less than 5 percent resulted in failure by surface welding.

Fretting occurs when two loaded, adjacent surfaces are free to experience a slight relative motion and are subject to vibration. Local stresses and concentrated friction phenomena combine to destroy lubricant-coatings and rapidly erode the metal surfaces. Godfrey and Bisson (ref. 15), NASA Lewis Research Center, investigated the use of MoS_2 to prevent fretting corrosion. Molybdenum disulfide was applied by six different methods. The most effective procedure was to burnish the surface of heated steel with a mixture of MoS_2 and syrup. This coating

delayed the fretting corrosion of a steel ball to 28×10^6 cycles as compared to 30 cycles for uncoated balls. This experiment consisted of vibrating steel balls against a glass plate which allowed observation of failure. Tests were repeated with vibrating steel flats in contact. Again, failure was delayed from 100 cycles to 10×10^6 cycles for the bonded coating. The role of the syrup is not completely clear, but under the conditions of application, the syrup probably carbonizes. This carbon may play a definite role in lubricating as well as bonding the coating to the steel surface.

Peterson and Johnson (ref. 16), NASA Lewis Research Center, continued further studies into the effects arising from method of application, contaminants upon the friction, and wear of low-speed, kinetic-friction parts lubricated with MoS_2. Frictional coefficients obtained for a purified grade of MoS_2 were found to vary by a factor of five (0.025 to 0.12) due just to the method of application. Contaminants naturally present from processing methods did not adversely affect the lubricating properties of MoS_2 in a significant manner except that 0.5 percent SiO_2 increased wear. Mixtures of 10 percent MoS_2 in oil gave lower frictional coefficients than either component separately; lower concentrations of MoS_2 in oil are, however, of questionable value.

Peterson and Johnson (ref. 17) also investigated various solids with lattice structures similar to those of MoS_2. Tests were performed in low-speed, high-load, frictional apparatus with the sample subjected to continuous sliding. The materials CdI_2, $CdCl_2$, PbI_2, $CoCl_2$, $AgSO_4$, $CuBr_4$, and WS_2 provided effective lubrication, but were no better than MoS_2. These results indicate that while low shear strength can be associated with structure, and is a necessary requirement, it is not alone a sufficient basis for selecting lubricating solids. The surface-energy relationships necessary to form an adherent film are also required for optimum results for solid lubricants. The results of the two studies just cited were jointly published by Peterson and Johnson (ref. 18).

HIGH TEMPERATURE LUBRICATION AND WEAR

NASA requirements for lubrication systems useful at higher temperatures have been increasing. The bearings of gas turbine engines operate at higher temperatures than do piston engines. The current development of liquid metal, heat-transfer systems, propulsion systems, and other applications are increasing the operational temperatures required for the sliding surfaces in bearings and seals. To meet these higher temperature requirements solid-coating lubricants are being studied and to date the results are particularly promising.

Peterson and Johnson (ref. 19) investigated the application of PbO, Pb_3O_4, Bi_2O_3, CdO, In_2O_3, WO_3, Sb_2O_3, and PdO as solid-film lubricants for use at temperatures up to $1,000°$ F. Oxides were a logical choice in

air operation due to their fully oxidized state. The particular oxides selected were those believed to possess low shear strengths. Experiments were conducted in low-speed, high-loading, sliding-friction apparatus up to 1,000° F. The results indicate that at 1,000° F lead oxide (PbO) was by far the most effective lubricant. The frictional coefficient was 0.09 for a PbO-lubricated-Inconel slider on an Inconel X disk. In the temperature range of 700 to 900° F PbO converts to Pb_3O_4 with increased friction coefficients. At room temperature, the frictional coefficients of PbO are greater than those usually acceptable for a solid lubricant.

Johnson and Sliney (ref. 20), NASA Lewis Research Center, studied high-temperature friction and wear properties of doped and undoped PbO coatings fused to steel. The effect of coating thickness, temperature, sliding velocity, run-in, and doping of PbO on the frictional coefficients and wear was determined. Results indicated that 1-mil-thick films were better than either thicker or thinner films. Small additions of SiO_2 and Fe_3O_4 decrease the volatility of PbO and inhibit its conversion to Pb_3O_4 at high temperatures. The appearance of PbO coated and uncoated bearings after a test of 1,000° F is shown in Figure 49.

The lubrication properties of bonded fluoride and oxide coatings for use in high-temperature environments were studied by Sliney (ref. 21), and Johnson and Sliney (ref. 24). Ceramic coatings of strontium fluoride with aluminum phosphate and fired-ceramic binders were not successful. However, ceramic-bonded, calcium fluoride-produced coatings exhibited frictional coefficients of 0.1 to 0.2 at 1,500° F. The most promising pro-
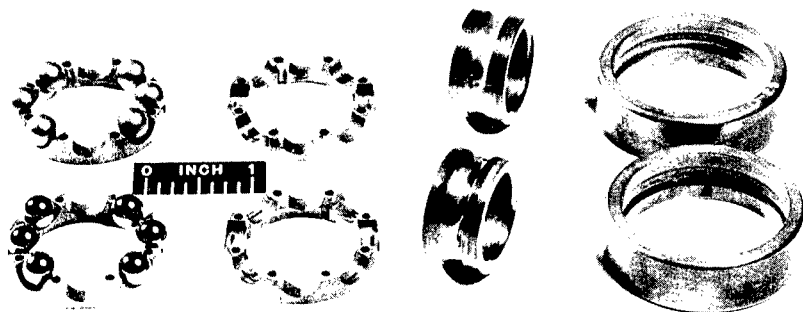

FIGURE 49.—Appearance of parts after 1,000° F test in an unlubricated 20mm-bore-bearing (top row) and a PbO coated bearing (bottom row).

cedure for application of calcium fluoride coatings consisted of spraying an aqueous suspension of a ceramic frit and calcium fluoride onto the substrate, drying, then firing to 2,200° F for 4 min. Finally, an overlay was applied with a flannel-covered polishing wheel impregnated with dry CaF_2.

Later, Sliney (ref. 22) extended the temperature range of calcium fluoride lubrication coatings to 1,900° F when used in connection with preoxidized substrates of Rene 41 alloy. The major CaF_2 coating was applied as a ceramic-bonded surface, but pure 0.2-mil-thick CaF_2 overlays improved the service life at the expense of a higher coefficient of friction. Increased loads reduced the coefficients obtained with overlays. The effects of CaF_2 coatings in reducing galling and local surface welding at high temperatures (1,900° F) were very apparent.

Blankenship (ref. 23), NASA Lewis Research Center, has been investigating the use of alumina and stabilized zirconia-coated dies with tungsten disulfide, boron nitride, and combinations of graphite and glass cloth lubricants for the extrusion of tungsten at temperatures above 2,500° F. Carbide-insert dies were originally used in the late 1950's for tungsten extrusion; however, die life was so short that the materials proved unsatisfactory. The current program was initiated in late 1960 when Mr. Blankenship learned of an Air Force (Wright Field) program at the TAPCO Division of the Thompson Ramo-Wooldridge Corp.

The Cleveland Hardfacing Co., using Rokide processes, prepared die coatings of alumina useful from 3,000° F to 3,200° F (see figure 50). Plasma-sprayed dies have also been used and evaluated. Zirconia has been tested to temperatures approaching 4,000° F. Lubrication studies have included the evaluation of numerous commercial high-temperature lubricants as well as a specially developed glass-graphite-layer lubricant. This latter material was prepared by gluing together a 10-mil-thick glass cloth and a 16-mil-thick WCB National Carbon Cloth, rolling to a 15 mils total thickness and then cutting to fit the die. Test results are currently being prepared for publication by Blankenship.

A general review of the NASA contributions to the field of solid lubrication coatings for high temperature service was also published by Bisson and Anderson (ref. 28). The importance of this work cannot be overestimated. While solid coatings are not widely used as lubrication systems the need for them is obvious, and the progress in attaining higher temperature limits serves only to encourage further work at an expanded level of effort.

BALL BEARINGS

Evans and Flatley (ref. 25), NASA Goddard Space Flight Center, studied the high-speed operation of miniature ball bearings in vacuum
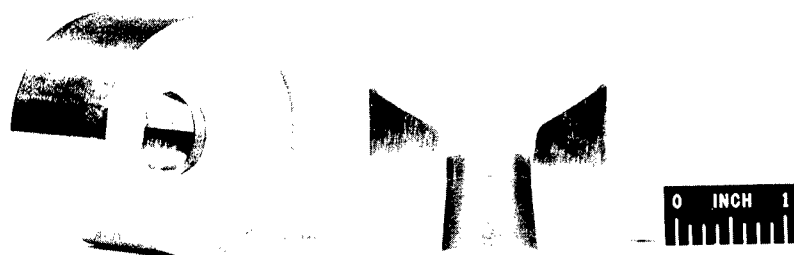
FIGURE 50.—Zirconia coated die used for the extrusion of 3,200° F tungsten.

with metallic-coating lubrication. Table 17 gives the complete listing of bearings used. Plate (A) was 23.88 carat gold with nickel, indium, and cobalt additives to improve adherence, hardness, and brightness. Plate (B) was almost 24 carat (pure) gold. Size R2-5 bearings were tested without external loading at 10,000 rpm with a goal of 1,000 hr life at a pressure of 10^{-7} Torr. The results indicate that: (1) thin metallic films as lubricants show real promise for space application; (2) gold with additives is superior to pure gold; (3) fully machined retainers provide good performance, and the use of relatively hard retainer materials extends useful bearing life; and, (4) bearing failures tended to be catastrophic, making predictions of the onset of failure difficult. The complete test runs are presented in table 18. Despite considerable scatter of the data, it is evident that the machined, silverplated circle C retainer material, using gold plate with additives, exceeded the test objectives in both runs. (One sample was withdrawn after 1,049 hr, but prior to failure). This study is continuing.

Demorest and McKannan (ref. 26), NASA Marshall Space Flight Center, are testing R-2 bearings in a screening program and have attained over 5,000 hr service using retainers machined from "teflon" filled with solid-film lubricants. During service the retainer is sacrificially worn away thereby renewing the lubricant. Gold, graphite, and MoS_2 are being studied to determine optimum combinations. Research on the use of MoS_2, WS_2, MoSe, and WSe as lubrication materials in vacuum is also being conducted.

The development of journal and ball bearings for space applications has made significant progress by exploring completely new materials and methods of application. However, a great deal remains to be accomplished in the perfection of inorganic-lubricant coatings, the development of design criteria, and failure statistics. While not a criticism of the quality of work, the statement is suggestive of expanded research and development programs. Further studies of the dynamic behavior of bearings in vacuum are of particular value in regard to the life of solid-film bearings since neither viscous gases or fluids are present to absorb energy. The work of Demorest and McKannan (ref. 27) suggests the need to test bearing materials for space applications on the basis of the internal damping capacity of various materials.

COMMERCIAL IMPLICATIONS

The contributions of NASA personnel and programs constitute an appreciable portion of the pioneering work in the technology of advanced lubrication systems. Today, the lubrication of gas turbines for commercial jet aircraft is not a major problem because the defense agencies and NACA supported the work responsible for the present state of technology.

The utility and importance of the NASA lubrication contributions requires an estimation of the rate of progress of specific technological developments. This is a particularly difficult project since it is difficult to judge the overall rate of growth for a technology, and usually impossible to earmark specific developments. The following factors should stimulate the direct use of space technology within the next ten years:

1. The increasing temperatures of power production systems necessary to achieve higher efficiencies.

TABLE 17.—*Bearings Employed in Phase I of the Study*

Retainer type and material	Gold-plating source		Number of bearings
	Balls	Races	
Machined, gold-plated silnic bronze	A	A	4
Do	B	B	4
Machined, 2.5 per cent beryllium copper	A	A	4
Do	B	B	4
Do	B	A	4
Machined, silnic bronze	A	A	4
Do	B	B	2
Machined, S-Inconel	A	A	4
Do	B	B	4
Machined, silver-plated circle C	A	A	4
Do	B	B	2
Do	B	A	4
Crown, 410 Stainless Steel	A	A	6

TABLE 18.—*Test Results from Phase I of the Study*

| Retainer type and material | Plate source | | Test | Life-time (hours) |
	Balls	Races		
Machined, gold-plated silnic bronze_____	A	A	1	369
			2	279
	B	B	3	39
			4	32
Machined, 2.5 percent beryllium copper_____	A	A	5	329
			6	12
	B	B	7	71
			8	4
	B	A	9	68
			10	6
Machined, silnic bronze_____	A	A	11	159
			12	80
	B	B	13	156
Machined, S-Inconel_____	A	A	14	873
			15	639
	B	B	16	178
			17	147
Machined, silver-plated circle C_____	A	A	18	*1049
			19	1660
	B	B	20	332
	B	A	21	136
			22	33
Crown, hardened 410 stainless_____	A	A	23	477
			24	142
			25	312

* Removed, before failure, after 1,049 hours testing.

2. The development of gas turbine engines for automobiles.

3. The impact of demands for higher performance from energy conversion systems.

4. Consumer demands for increased reliability of products.

5. Consumer desires for products which require less service and have lower maintenance costs.

The importance of NASA contributions to lubrication technology is evident from the attention given by industrial concerns to NASA information published in the technical literature. The extent of the attention shown is a good measure of the extent and importance of NASA work programs and results.

The quality of NASA published papers is above average judged by their contents and presentation. However, based on the quantity of work, it seems more economical to expand NASA research for solid lubricants investigations rather than to depend on future crash programs.

Thermal Insulation Coatings

GENERAL AEROSPACE TECHNOLOGY

One useful index to the technological progress achieved by an industrial society is the amount of energy generated and consumed per inhabitant. However, a more rigorous test of technological affairs is the quantity of energy released and controlled per pound of engine. With advanced technology, more energy is produced per pound of engine; thus, a 170-pound man may produce at the rate of less than one horsepower, and a 170-pound solid fuel rocket can produce a directed thrust of at least 1,000 times as great. Although we shall not consider hydrogen weapons, even for these a greater energy release is possible although the control of such energy levels in engines is questionable.

As a general rule, increased rates of energy release require higher temperatures. The kinetic energy of a molecule increases as the square of its temperature. Although this relationship between kinetic energy and temperature tends to limit required temperatures, the useful temperature boundaries of most materials, particularly metals, have been reached. Thus, increasing power-versus-weight requirements have given rise to the development of a host of inorganic coating applications with concern to their thermal insulation properties. In general, because inorganic or ceramic materials are brittle when used in the usual polycrystalline form, they are unsuitable for applications requiring tensile properties. However, metals which can support tensile loading exhibit a marked decrease in strength with increasing temperature. The use of inorganic thermal insulation coatings depends on the application of the best properties of the coating and substrate. The demands for such thermal coatings for NASA applications will increase.

To detail the significance of coatings a review of the two most important application areas, aerodynamic heating and rocket engine uses, will be discussed in a general way. The specific applications represent different demands which can be quite exacting, but a general review will provide a suitable background of the major problem areas. For the materials-oriented, technical person interested in this highly complex field, an excellent introduction is provided by Pellini and Harris (ref. 1). Their
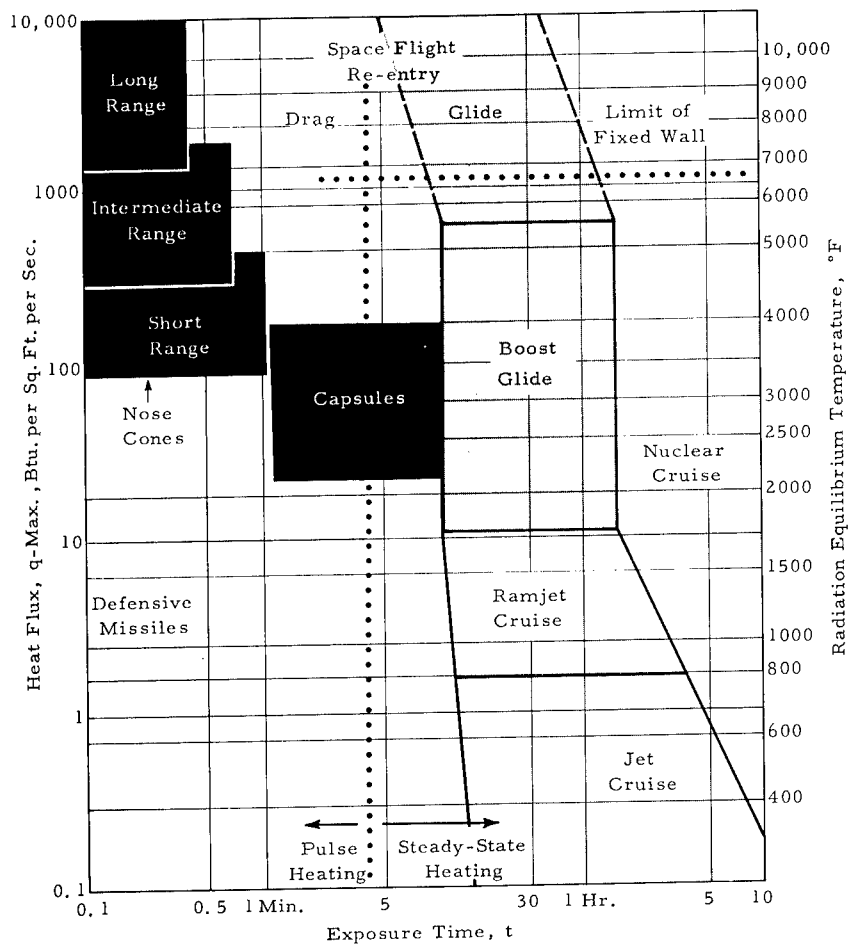
FIGURE 51.—The environmental conditions of various classes of vehicles under conditions of steady-state heating (right) and pulse heating (left). The lines defining the vehicle zones are not rigid boundaries but indicate generally expected locations.

paper resulted from a staff study supported by the National Academy of Science Materials Advisory Board and the Office of the Secretary of Defense.

Figure 51 presents the time, temperature, and exposure of materials associated with various types of missiles, spacecraft, and aircraft. For example, long range missiles upon re-entry are subjected to heat fluxes up to 10,000 Btu/ft²/sec for periods up to 30 seconds. While at the other extreme the supersonic transport will cruise at speeds of Mach 3 and be subjected to 1 Btu/ft²/sec for periods of 1 to 2 hr. To meet such diverse requirements, different methods will be required for different conditions.
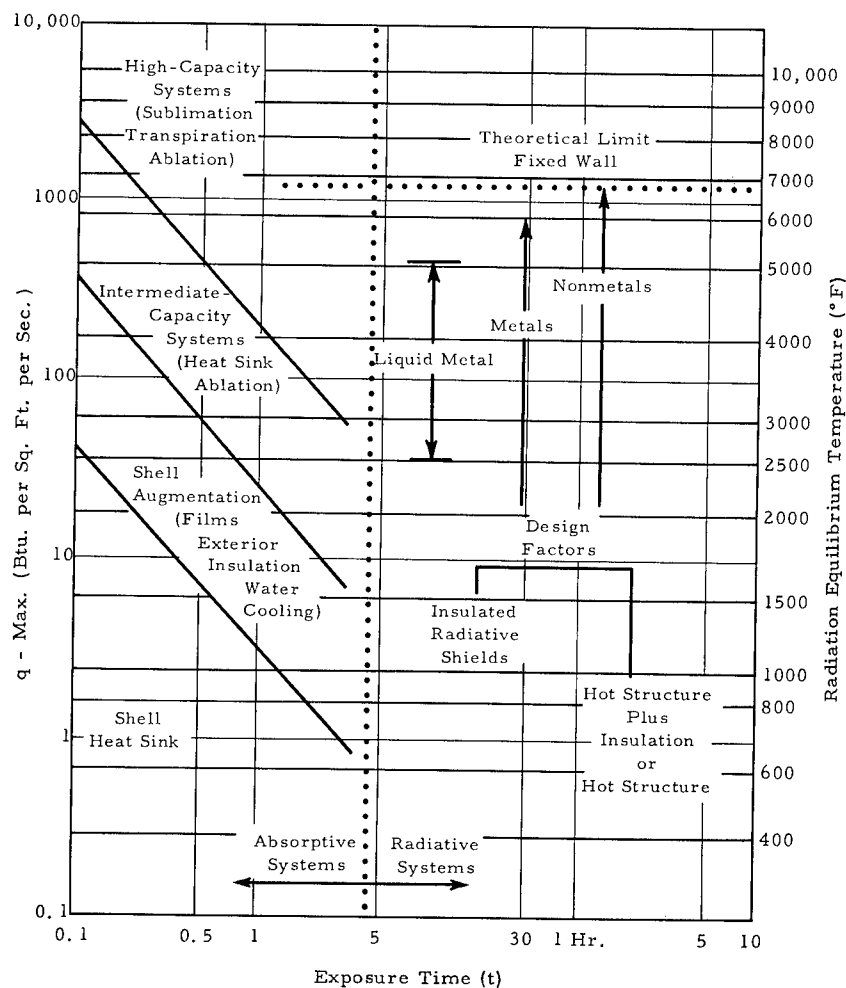
FIGURE 52.—Applicability of the various types of thermal protection systems. The delineation is not a rigid one but is intended to represent the most likely areas of use for each system.

Thermal protection systems may be classed as absorptive or radiative. Figure 52 indicates that the radiative systems are generally useful for time periods longer than five minutes and absorptive systems for shorter periods.

Within the absorptive systems are subsystems of the sublimation, ablation, transpiration, and shell-heat-sink types. This group of subsystems is currently the most highly developed and perfected as a consequence of the requirements for the protection of nuclear weapons delivered by long, intermediate, and short range rockets. Within this
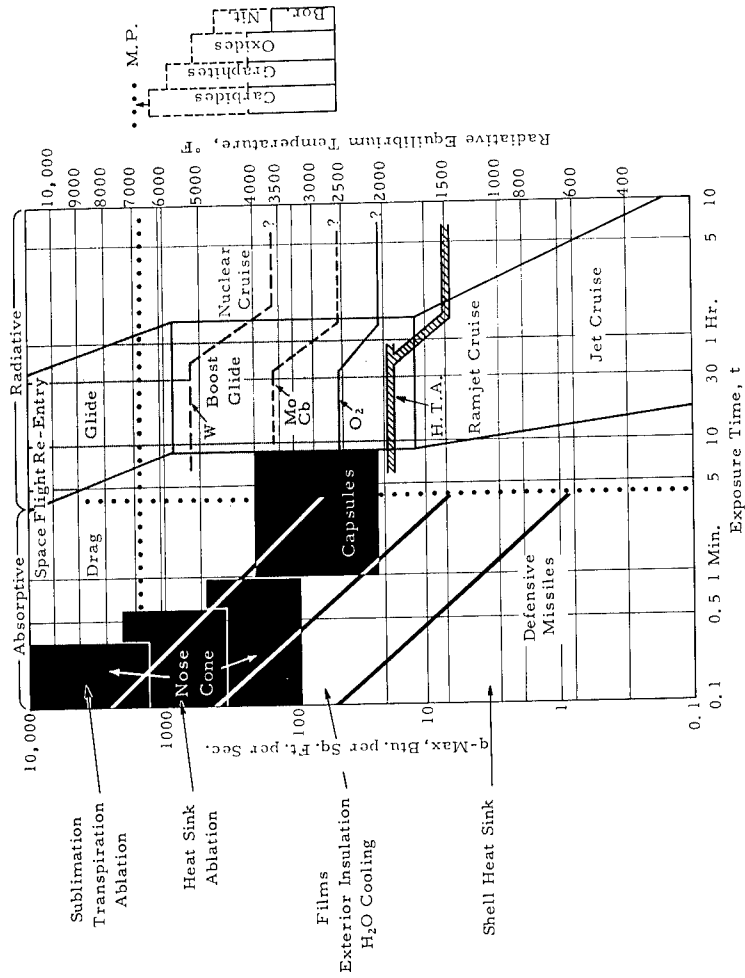
FIGURE 53.—Evaluation of the problems of material selection for thermospheric flight.

region must be classified the NASA ablation system used for the protection of the successful Mercury orbital and suborbital flights.

Insulating coatings, however, are primarily useful in the steady-state, radiative systems. In figure 53 it is apparent that the maximum steady-state, radiative system, temperature limit is imposed by the highest melting point of solids. Perhaps in the future electromagnetic forces can be utilized to retain liquids on surfaces such as radiative surfaces, but for the present we must limit our discussion to solids.

Hot structures, and hot structures plus insulation were defined by Pellini and Harris as those systems which allowed the load-bearing structure to become heated, while the insulation was used only to protect the payload. The insulated radiative shield concept interposes insulation between the aerodynamic surface and the cold structure. The strength-to-weight ratio is the major criteria for the design of these systems and the operating regimes indicated in figure 52 are the best current estimates. The rate at which specific materials are developed will determine the exact interface between alternate problem solutions. Even though the situation is in a state of flux, the continued development of suitable insulations, both of the bulk and coating types is required.

The insulation coatings which NASA is currently developing are useful for the lower temperature areas; though, undoubtedly, materials useful for higher operating temperatures will be a necessity as the less rigorous requirements are met.

When power is absorbed as in the heating of aerodynamic surfaces, the power must be generated within power plants using even higher temperatures; thus the very presence of external aerodynamic heating indicates even more severe internal heating. Thermal insulation coatings are required for turbine-jet engine afterburners, ram-jet engines, solid propellant rocket nozzles, liquid rocket engine combustion chambers, and guide vanes.

Fundamental requirements for insulation coating materials are: (1) high melting point; (2) low density; (3) high surface emissivity; (4) high thermal shock resistance; (5) low vapor pressure; and, (6) resistance to oxidation or chemical environment. Other important factors involve cost, ease of repair, adherence, etc., which must be evaluated against the services received from a particular application. The principles utilized in the development of insulating coatings for NASA requirements are in a technical sense universally applicable, but not necessarily so in an economic sense.

UNFIRED CERAMIC INSULATING COATINGS

REFLECTIVE FIBROUS INSULATING COATINGS

Coating Requirements

Gimbals and supporting structural members in areas immediately adjacent to rocket engines must be protected from heating. This is an increasingly severe problem particularly as larger multiengine rockets are developed. The Saturn C–1 cluster of eight H–1 engines (188,000 lbs. thrust each) imposes a 3,600-Btu/ft² heat load of which 60 to 80 percent is direct thermal radiation from the rocket plume with convection accounting for the remainder. A noninflammable, air-cured, low-conductivity coating capable of protecting the base rocket structure from temperatures exceeding 300° F under the imposed heat load for periods of approximately 145 sec was required.

A coating system meeting these requirements was developed at the NASA Marshall Space Flight Center by Vaughn F. Seitzinger (ref. 2). The basic honeycomb-sandwich construction selected for this study utilized 10-mil-thick face sheets and a 1-inch-thick honeycomb core having ¼-inch-square cell openings and a wall thickness of 2 mils. The components were fabricated from a high-strength stainless steel and joined with a silver-brazing alloy. A 190-mil-thick honeycomb reinforcement core, having ½-inch-square cell openings and a wall thickness of 2 mils, was brazed to one face of the basic honeycomb structure to serve as a mechanical device for bonding the insulation. The basic honeycomb structure including the reinforcement core weighs approximately 1.6 lbs/sq ft. The fibrous insulation material consists of fibrous potassium titanate, asbestos and colloidal silica placed into the honeycomb. A protective nitrocellulose coating preserved the surface of the insulation from contamination and optical-properties alteration until usage at which time the nitrocellulose was burned off without leaving any residue.

The honeycomb structure provided means for mechanically attaching to the rocket structure. In addition the honeycomb increased the mechanically contacting interface between the substrate and the coating. Mechanical interlocking is accomplished by passing the honeycomb through rollers which crushes the structure and provides re-entrant surfaces for solid mechanical interlocking much like a jigsaw puzzle is held together (fig. 54).

The low density, low thermal conductivity, inorganic, fibrous filler provides the required insulating properties. The total heat load imposed on the rocket structure is a function of the coating thermal diffusivity and thickness as well as the maximum surface temperature. Since the major thermal flux to the coating surface is by radiation, a highly reflective insulation is desirable. High reflectivity will limit the effective heat flux to and the temperature attained by the coating surface. However, no
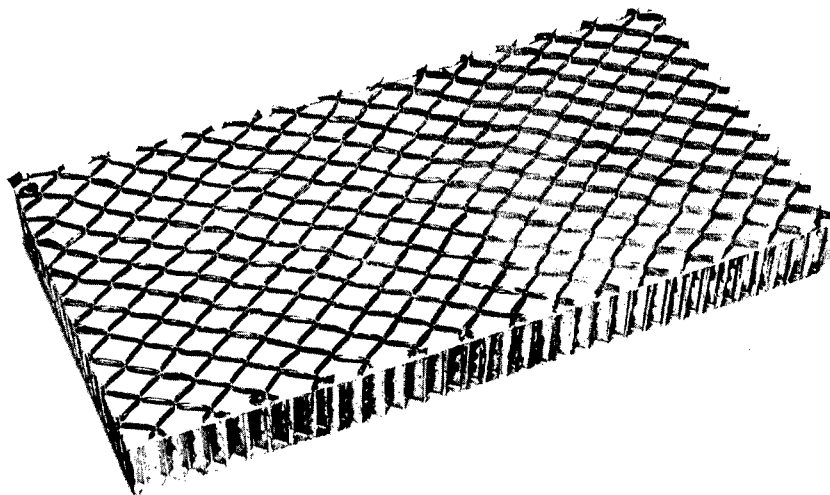
FIGURE 54.—Honeycomb sandwich construction with and without open-faced core crushed.

known material has a sufficiently high reflectivity so that it need not be backed up by an insulating layer.

Reflective Coating Composition

The basic fibrous insulating material is a fiber form of potassium titanate produced by Du Pont "Tipersul" (ref. 3). The block form of "Tipersul" contains approximately 10 percent of H. I. Thompson Fiber Glass Company's Refrasil fibers and probably some organic binders. Refrasil is composed primarily of refractory silicate fibers. Organic binders were burned out by heating the block "Tipersul" at 1,000° F for 4 hr in air. The basic properties of fibrous potassium titanate are shown in table 19. Other fiber materials were investigated; however, potassium titanate fibers proved superior. The fundamental explanation for this superior performance can be given in terms of Klein's (ref. 18) equations (NASA Ames Research Center) which give a rigorous treatment of radiant transfer to a material possessing both optical scattering and optical absorption. Radiant transfer to such a system depends on the scattering to absorption ratio. Potassium titanate fibers possess a high reflectivity since they are quite small fibers and have a high index of refraction and a low absorption coefficient.

Sodium silicate, monoaluminum phosphate, colloidal alumina (Baymal) and colloidal silica were tested as binders. Sodium silicate was unsatisfactory because it required too high a setting temperature and was not sufficiently refractory. Monoaluminum phosphate formed an excellent

TABLE 19.—*Fiber Properties of Fibrous Potassium Titanate*
E. I. du Pont de Nemours, Inc.
"Tipersul"

Average diameter (μ)	1
Length after dispersion (mm)	0.2–0.5
Melting point (° F)	2,500
Theoretical density (lb/ft³)	225
Calculated specific heat (Btu/° F/lb)	0.22
Hardness (Mohs)	4.0
Approximate chemical composition	$K_2Ti_6O_{13}$

bond and was sufficiently refractory. Unfortunately, it reacted with the steel honeycomb structure. Colloidal alumina did not provide a useful bond at the curing temperature desired. All three of these bonding materials were not resistant to a moisture resistance test.

Colloidal silica, Du Pont's 30 percent solids Ludox HS, proved to be the superior binder due to its ability to form a strong moisture resistant bond at 180° F. "Tipersul" bonded with colloidal silica cracked during firing due to excessive shrinkage. Additions of asbestos cut to $\frac{1}{2}$-inch lengths practically eliminated this problem. The final batch composition designated M–31 is given in table 20.

TABLE 20.—*Batch Composition of M–31*

Material	Parts by weight
Tipersul block	90
Cut asbestos	10
Ludox HS	420

The cut asbestos fibers and "Tipersul" were blended together and the colloidal-silica binder added to produce a workable mixture. The moist mixture was trowelled and rolled to about a $\frac{1}{2}$-inch-thick layer which filled and interlocked to the honeycomb structure. Panels were dried over a period of 12 hr at a temperature of 180° F. After drying, three coats of nitrocellulose containing 12 percent nitrogen dissolved in methyl-ethyl-ketone were brushed on the insulation surface to provide a protective coat (fig. 55).

Coating Properties

The rupture strength, density, and thermal conductivity of colloidal-silica bonded fibrous mats proved usefully nonisotropic with coating thickness. Because drying occurs only from one surface, some of the colloidal silica migrated with the moisture to the outer surface of the coating. Consequently a density gradient shown in figure 56 resulted. This produced a dense, strong, and hard outer surface with a very
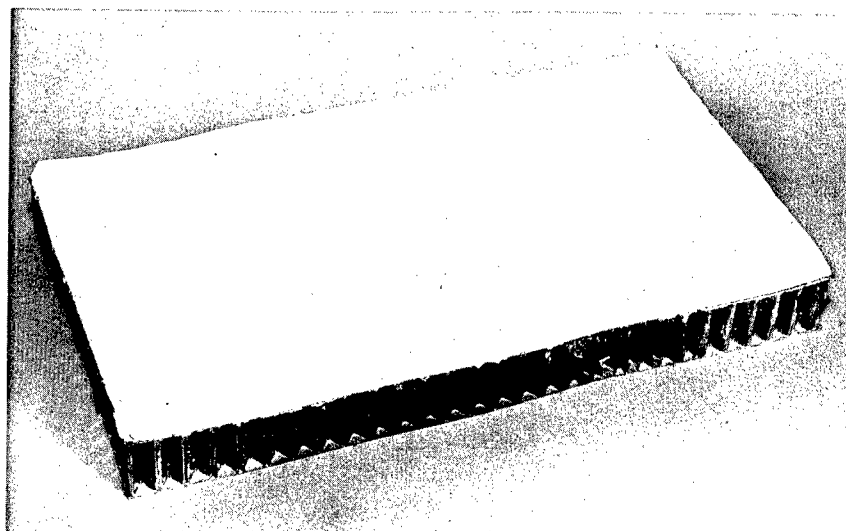
FIGURE 55.—Honeycomb sandwich construction with M-31 insulation applied.

desirable protective outer layer, while maintaining a less dense, lower thermal diffusivity inner layer.

Modulus of rupture and modulus of elasticity of the coating are given: (1) as prepared; (2) after soaking in water for 200 hr (both wet and dry); (3) boiled for 3 hr and dried and with the load applied from the rear surface. The results are shown in table 21. The strength of the outer surface is more than twice the inner surface, and water soaking or boiling does not seriously affect the mechanical properties.

TABLE 21.—*Mechanical Strength of M-31*

	Rupture modulus (psi)	Young's modulus (psi)
As prepared	475	250
Soaked in water for 100 hr		
Tested wet	370	200
Dried	480	250
Immersed in boiling water for 3 hr and dried	485	270
Load applied from back side (to determine effect of dense outer layer)	1,075	260

The spectral reflectivity from 0.3 to 3.0μ is given in figure 57 and the spectral emittance from 3.0 to 14.0μ in figure 58. Data was not taken in the 3.0 to 4.0μ region and the presence of the water bond there probably results in a lower reflectivity than is shown in figure 58 for this region.
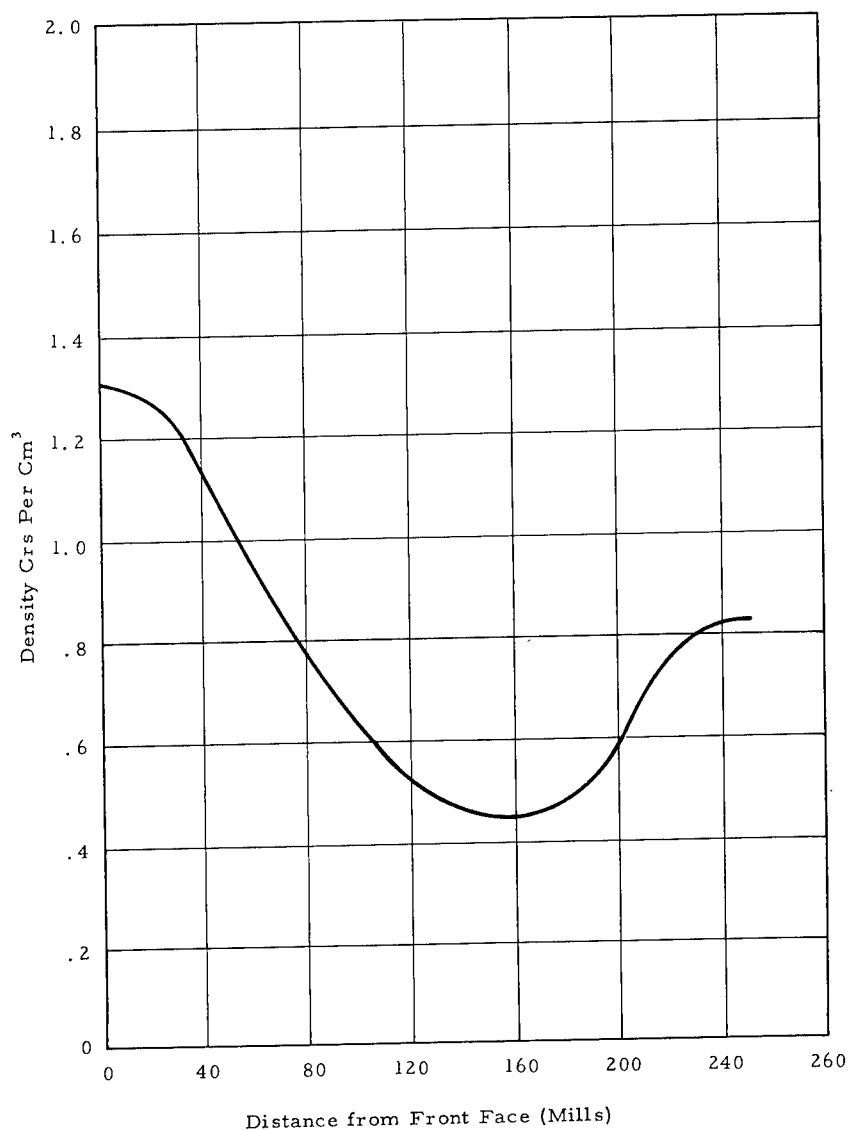
FIGURE 56.—Density gradient through a ¼-inch-thick specimen of M–31.

In general, the reflectivity is reasonably high over most of the spectrum particularly in the visible region.

Thermal conductivity data for the M–31 coating are shown in figure 59. The thermal conductivity is quite low for insulating materials of comparable strength and rigidity.
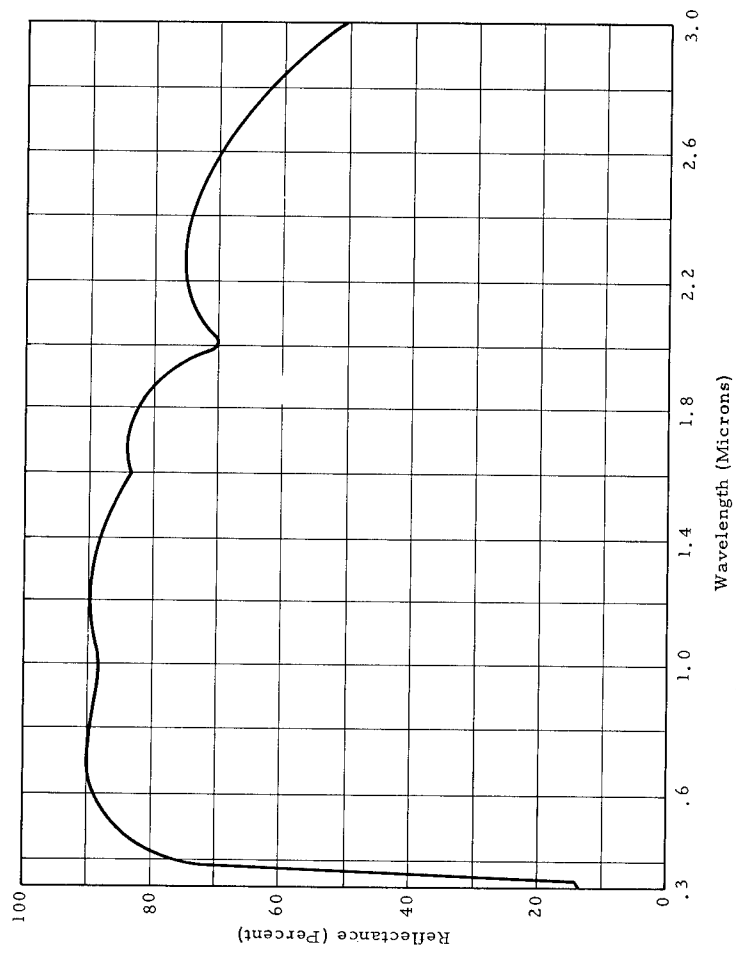
FIGURE 57.—Absolute spectral reflectance of M–31.
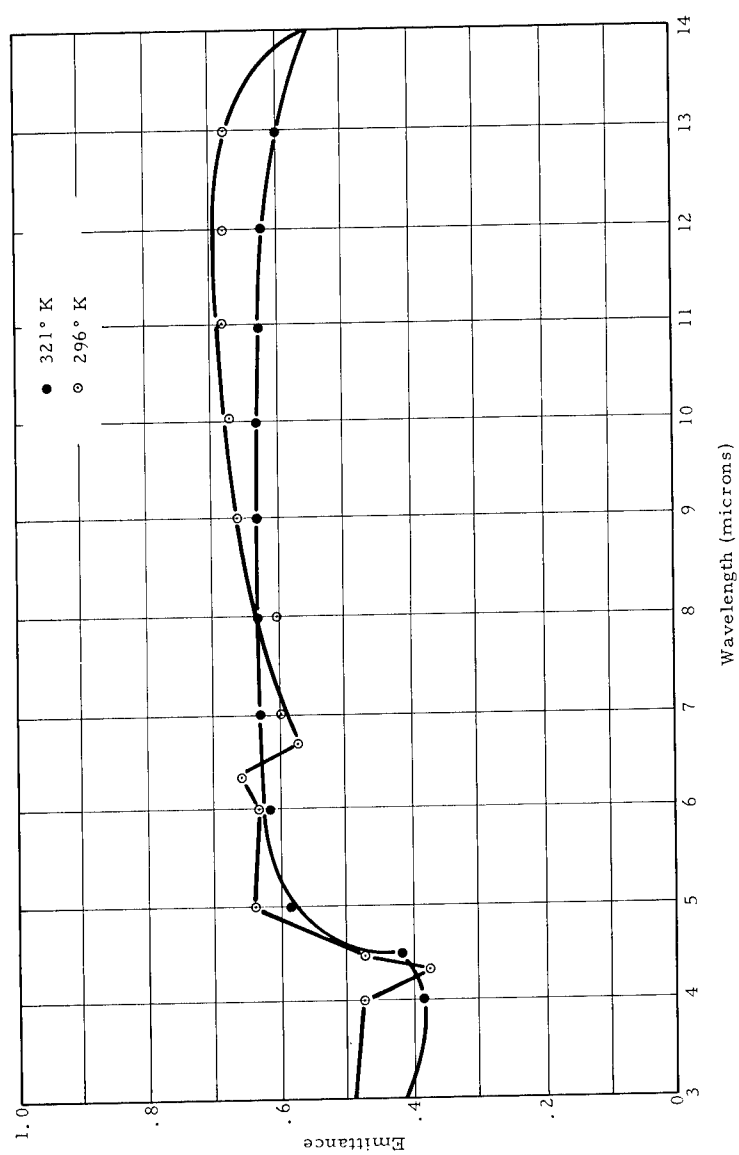
FIGURE 58.—Spectral emissivity of M-31.
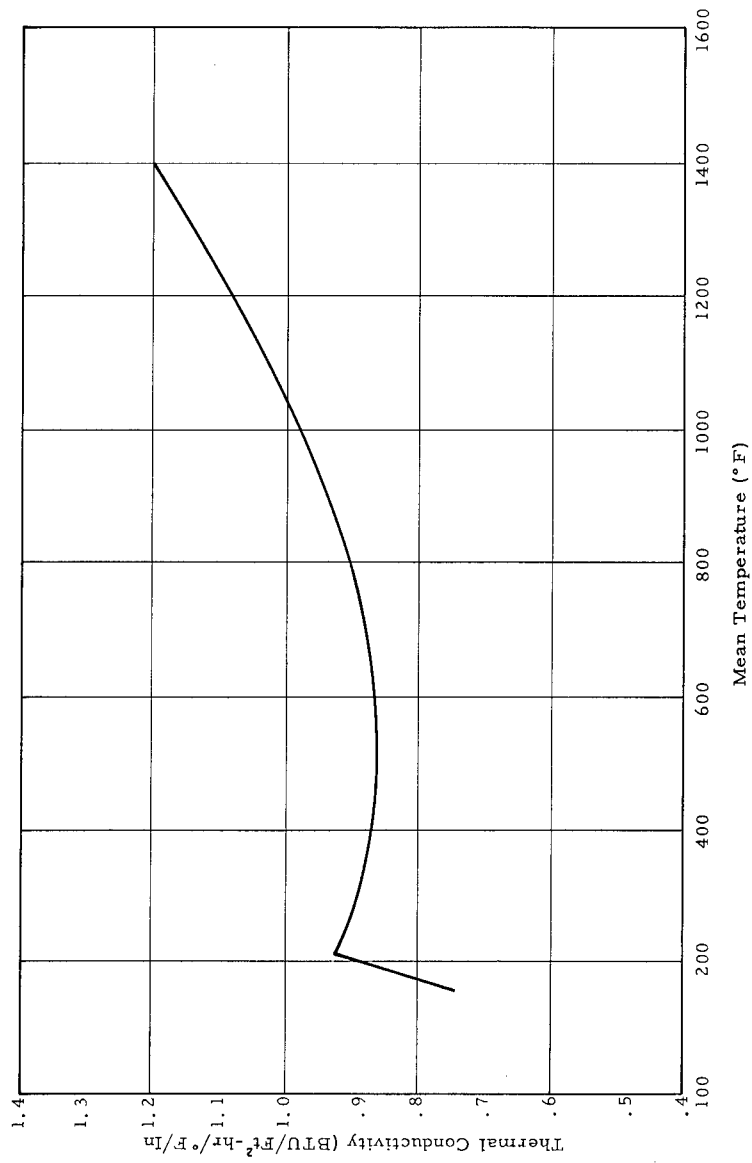
FIGURE 59.—Thermal conductivity of M–31.

Coating Performance

A 0.320-inch-thick coating was not affected by a 24-Btu/sq ft/sec radiant flux for 145 sec. Specimens did not fail in test until subjected to a 72-g vibration.

ALUMINUM PHOSPHATE INSULATING COATING

An aluminum phosphate coating suitable for application by dipping, painting or spraying onto stainless steel and nickel-base alloys was developed by Eubanks and Moore (ref. 4) under NASA sponsorship. This coating differs in a significant manner from the numerous other phosphate coatings, cements and castables, by using −325 mesh hydrated alumina in place of aluminum oxide to react with phosphoric acid to form the aluminum phosphate cement. Aluminum phosphate binders can be mixed with almost any oxide particle to form the final insulating coating. Usually alumina or calcia-stabilized zirconia are used. Zirconia is preferred for many applications because of its lower thermal conductivity and higher melting point.

Aluminum phosphate binders prepared with hydrated alumina can be cured by a 400° F heat treatment, though higher temperatures increase the strength and chemical resistivity of the coatings. After curing, the maximum-use temperature is similar to other aluminum phosphate binders, which for some applications is 3,500° F with alumina and 4,000° F with zirconia.

ALUMINUM PHOSPHATE FOAMED-IN-PLACE INSULATOR

Eubanks and Hunkeler (ref. 5) of the NASA Goddard Space Flight Center developed a novel and useful aluminum phosphate insulation which, because of its physical and chemical properties, can be foamed in place and cured at low temperatures. Essentially, this material is an aluminum phosphate prepared from hydrated alumina of the same type as described above, but into which is mixed a fine metal powder (ref. 6). During the setting of the phosphate, the acid reacts with the metal powders to form hydrogen gas which bloats the mass forming a lightweight insulating material of controllable size and quantity of discontinuous pores. The insulation is useful to temperatures of 3,500° F.

Foamed-in-place insulations are prepared from compositions shown in table 22. These constituents are mixed together as a slurry in a suitable container by stirring before pouring into an enclosure of the shape for which an object is desired. This material is also being used as a potting compound to protect electronic components from vibration and heat. When the slurry comes in contact with metals it will usually react and corrode them because the pH is about 3.0. However, it is quite simple to paint or spray metal surfaces with a thin protective plastic film to prevent the attack.

TABLE 22

Ingredient	Amount %
Orthophosphoric Acid (85 percent)	35–55 Wt.
Al(OH)$_3$ • nH$_2$O	35–55 Wt.
Bentonite	1.5–4.5 Wt.
AlPO$_4$	0–15 Wt.
Metal Powder[a] (−150 to −325 mesh)	0.1–0.7 Wt.
Silica, Colloidal[b]	0–5.0 Wt.

(a) Any metal which will react with phosphoric acid to form gas may be used. Aluminum, magnesium, tin, and zinc were experimentally tested.

(b) "Cab-O-Sil" manufactured by the Cabot Co., Boston, Mass., was used in this study.

Investigations of this material are still in progress; however, Eubanks (ref. 7) has supplied the following information.

Control of Porosity and Density

These properties can be controlled quite accurately by varying the aluminum metal powder particle size and content. The pore size is controlled by the metal particle size, while the porosity and bulk density are independently controlled by the amount of metal powder added. It is possible to vary the total porosity of the material from approximately 5 percent to 90 percent by volume with a corresponding density variation of 140 lb/cu ft to ˙˄ lb/cu ft.

Curing Time vs. Temperature

The foam can be cured at any temperature between 65 and 100° C. The time required for curing is a function of the temperature, the size of the foamed article, and the curing environment. If the foam is enclosed in a mold during the entire curing period, as much as 24 hr are needed at 65° C and about 12 hr at 85° C. If the mold cover is removed or the piece is taken out of the mold entirely after the first ½ hr of curing, approximately 8 hr are required at 65° C or 3 to 4 hr at 85° C.

Thermal Conductivity.—The thermal conductivity is quite low as evidenced by a torch test using a potted carbon resistor. Quantitative values, however, have not yet been obtained.

Thermal Shock.—Specimens were thermally shock tested by heating them to 500° C (932° F), 1,000° C (1,832° F), and 1,500° C (2,732° F) and immediately immersing them in water at room temperature. No change or degradation of the material was noted after this experiment.

Tensile Strength.—No data.

Compressive Strength.

Density (lb/ft³)	Compressive strength (psi)
20	120
27	270
37	600
50	2,400
90	6,200

Electrical Conductivity

Because of the high porosity of the foamed material and its ceramic nature, the electrical conductivity of the material is undoubtedly quite low. Quantitative data, however, have not yet been obtained.

Water Solubility

After 7 hrs in boiling water the weight loss was 0.01 lb/lb. The solubility in stirred water at room temperature revealed approximately the same weight loss.

Colorability

The material is susceptible to color additives. Small percentages of the standard second-phase, ceramic-coloring materials (chromium oxide for green, iron oxide for beige, etc.) can be added to the basic mixture producing a permanent insoluble coloring effect.

Adhesive Properties

The material can be cemented with alundum cement; Sauereisen cements (P–1, P–78, P–7), which are high-temperature cements; ordinary brick mortar; and most other cementing compositions.

Machinability

The material is easy to form. It can be cut with a hacksaw, shaped with a wood rasp, ground on an abrasive wheel, etc.

HIGH-TEMPERATURE INSULATING CERAMIC FOAMS

The investigation of high-temperature, insulating, ceramic foams is being conducted by the Materials Division of NASA under Contract NASr–99. The development of lightweight, porous, ceramic foam materials especially designed for high-temperature insulations was described by Hessinger (ref. 8). In addition to the development of materials, an investigation of radiant-transfer mechanisms within solids at temperatures over 3,000° F is being undertaken.

Stabilized-zirconia foams ranging from 10 to 15 percent of theoretical density have been prepared by mechanical foaming techniques. Flexural strengths measured at room temperature ranged from 3,500 to 5,200 psi for materials containing nominal pore sizes of 200 to 300μ. Most test data were obtained using foamed samples of 13 percent theoretical density
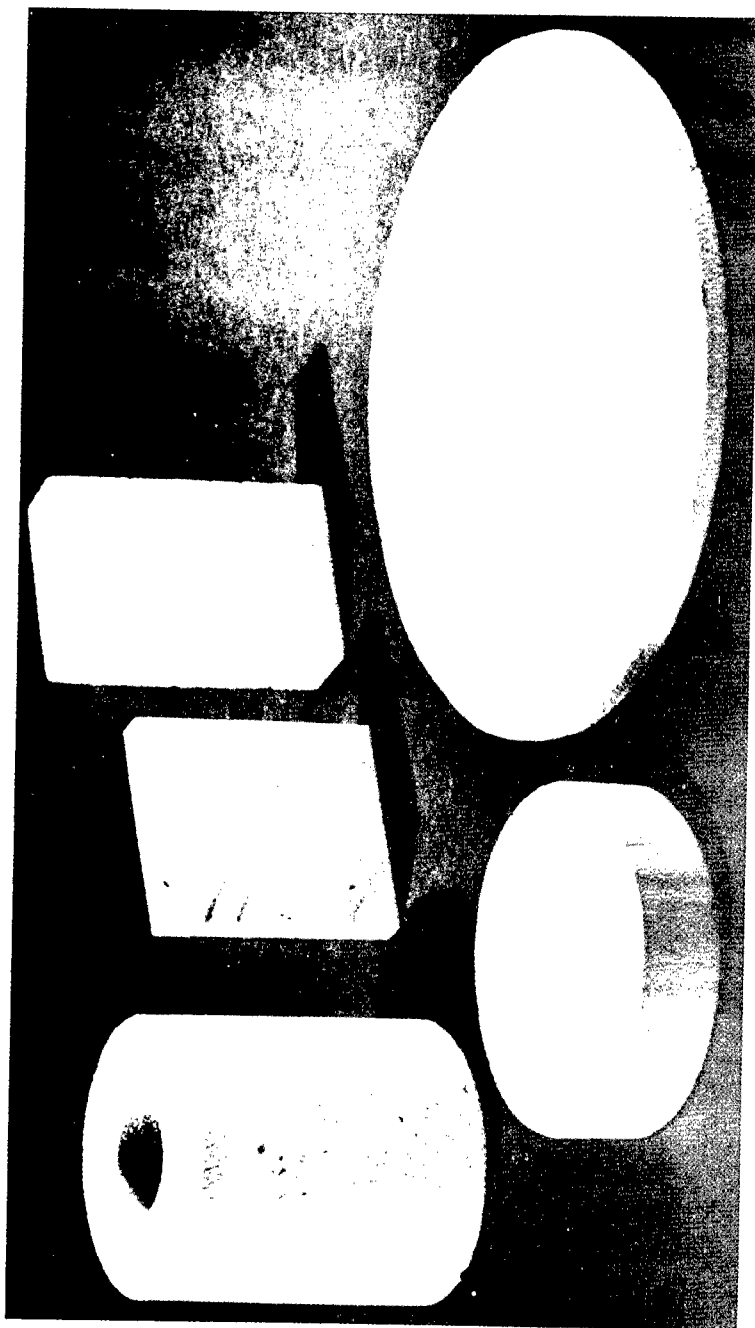
FIGURE 60.—Foamed zirconium oxide ceramic bodies. Section of thermal conductivity test specimen at upper left.
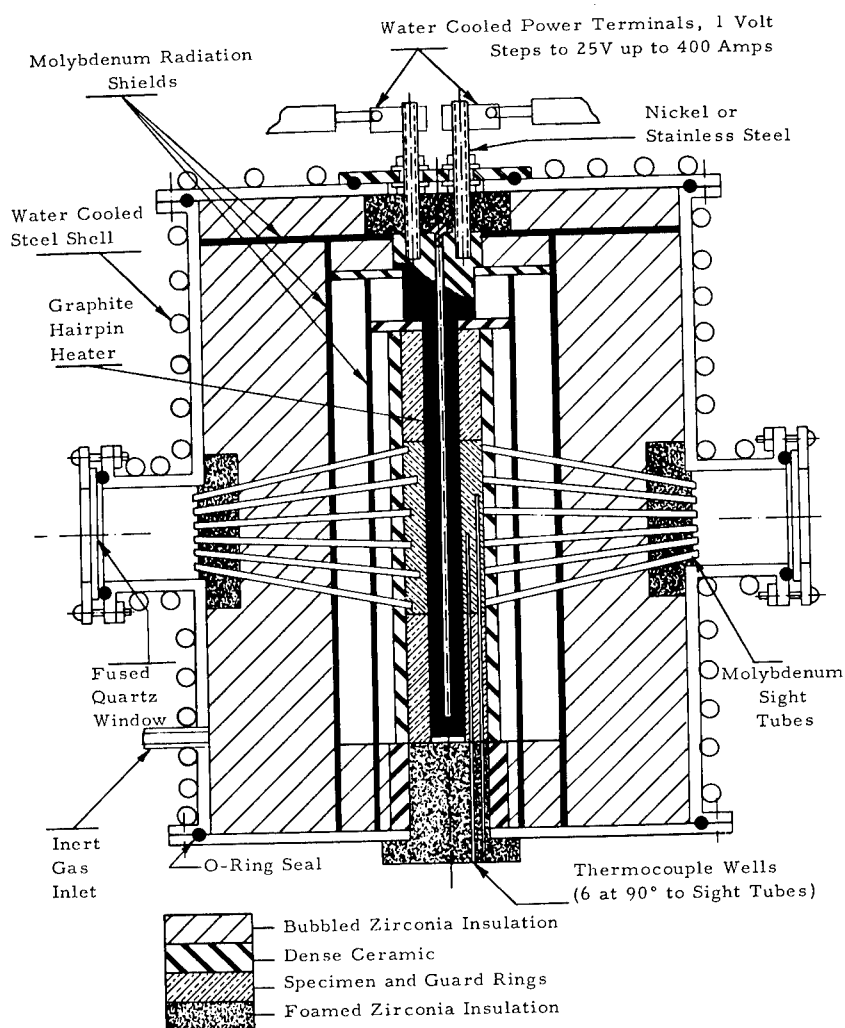
FIGURE 61.—High-temperature thermal conductivity apparatus.

(0.85 to 0.90 g/cc).   Typical foamed-zirconia shapes are shown in figure 60.   Foamed samples were impregnated with carbon, graphite, tungsten flake, molybdenum metal, and tungsten-coated zirconia spheres.

Apparatus to measure the thermal conductivity of foamed materials under inert gas or vacuum has been developed and operated to 4,300° F. This apparatus (fig. 61) is a radial heat flow method which utilizes a cylindrical specimen 2 inches O.D. by ¾ inch I.D. and 9 inches long. Temperature measurements are made optically by sighting down molybdenum sight tubes located in the radial direction and spaced along the
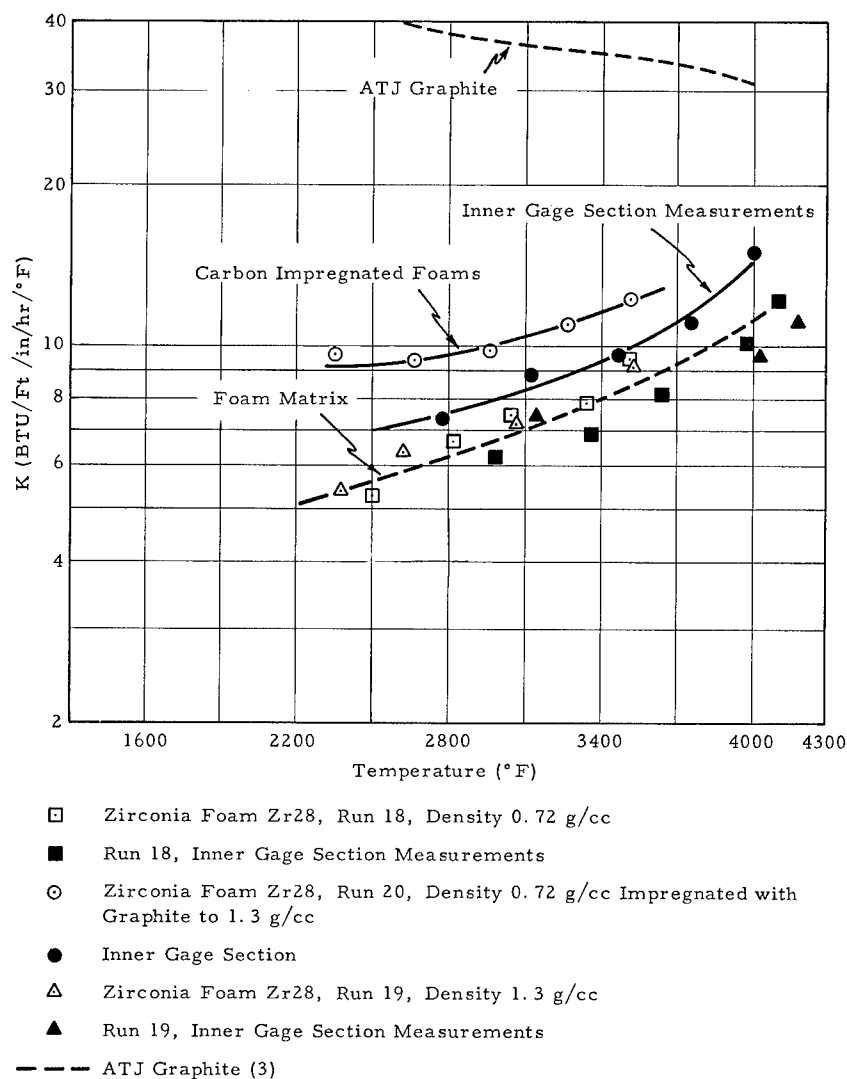
FIGURE 62.—Thermal conductivity measurements on composite zirconia foams.

specimen axis. Actually, two sets of sighting tubes are used; one set views the outer surface of the sample at uniformly spaced points, and a second set mounted 180° around the specimen is arranged so that the ends terminate at different depths within the sample. In addition, for lower temperature measurements, axial thermocouples are mounted in the sample. The heat-flux is estimated by assuming that the power is generated uniformly along the length of the graphite electrical resistance heater.

Thermal conductivity data taken for carbon-impregnated and unimpregnated zirconia foams are shown in figure 62. These data represent initial results and perhaps should be considered tentative. Some error may be present due to the location of sight tubes along temperature gradients. Usual practice dictates that temperature measurements be made along isotherms, if possible. Carbon-impregnated foams appear to have conductivities of 9.0 Btu/ft/in/hr/°F at 2,500° F, which is approximately twice that of the basic foam matrix at the same temperature. However, the slope of the conductivity-versus-temperature curve is less for the carbon-impregnated material and a cross-over point with respect to the unimpregnated foam may occur at temperatures above 4,000° F.

The data must be used with care since the presence of a graphite heater at elevated temperature, even though not directly in contact with the foam sample, is likely to alter the oxygen-defect concentration at temperatures above 2,800° F. Plunkett and Kingery (ref. 9) presented results obtained for the emissivity of zirconia under similar experimental conditions in which the total normal emittance increased from approximately 0.4 to 0.9 at this temperature due to the generation of oxygen defects. The overall effect of oxygen defects on thermal conductance at high temperature is not known since a number of unknown factors are present. The increase in oxygen defects could provide a mechanism for the reduction of energy transport by decreasing the radiant transfer through the solid by limiting the optical mean free path. On the other hand, due to increases in emittance, radiation across the pores will increase effective conductivity. The net effect will depend on the amount and nature of pores, the conductivity of the solid and the absolute temperature. For applications in air or oxidizing atmospheres, data taken in carbon- or graphite-containing equipment must be used with caution.

CERAMIC THERMAL INSULATION COATING FOR MACHINE WELDING HOLDING TOOLS

During the machine welding of high strength-to-weight ratio materials, chill bars are used to rigidly hold the pieces to be welded and simultaneously to limit temperature build-up in the material adjacent to the weld area. Chill bars consist of a high-strength, high thermal conductivity, copper, backup bar and two hold-down fingers as shown in figure 63.

The overall heat transfer situation at the weld zone is complicated and heat losses occur by gas convection, and by radiation from the weld zone as well as by thermal conduction out through the weld piece to the chill bars. In the region of the chill bars, heat is transferred across the contact area between the weld piece and the chill bars. The generation of a uniform, high-strength weld requires a careful balance between thermal input power and thermal losses. In general, welding machines
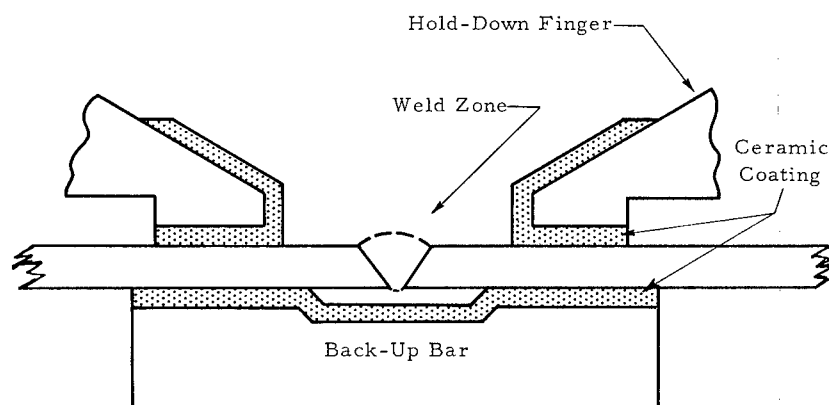
FIGURE 63.—Ceramic coating to provide thermal insulation for welding tooling.

are regulated to provide constant power input; thus, in order to generate satisfactory welds, thermal losses must be held constant. In general, the convection losses and radiant transfer from the weld zone are solely a function of temperature of this zone; consequently, if the weld area tends to overheat, these thermal losses increase, and to some extent, are self-regulating.

The heat transfer to the chill bars is more complicated. The high conductivity materials used in the holding apparatus and their nearness to the weld zone assures maximum thermal transport which is mainly a function of temperature. However, the thermal contact resistance of the interface between the weld piece and the holding apparatus is highly variable and depends upon the parameters of applied pressure, surface roughness of the pieces, tool and part tolerances, parts contours, and warpage during welding. Usually, applied pressure is held constant; however, the other parameters are subject to sizeable variations which are difficult to control. Consequently, when thermal contact resistance increases, the temperature of the weld zone, the width of the bead, and the amount of drop-through also increase, and a "hot-spot" results. On the other hand, a decrease in contact resistance results in a "cold-spot" which is evidenced by a decrease in bead width. Such fluctuations give rise to nonuniform welds of lower strength, and local buckling of the weld piece.

Since the problem has plagued the welding industry for years, various methods have been tried to reduce or eliminate the difficulty. Two different approaches were tried: (1) use of various holding-device materials having different thermal conductivities, and (2) use of extremely accurate tooling with rigid tolerances maintained by frequent tooling replacement. Neither of these approaches has proven to be a suitable answer in that they were expensive and generally unreliable.

Calfee and Lodermeir (ref. 10) of North American Aviation, Inc., working under NASA Contract NAS 9–150, developed an entirely new approach to the problem. The hold-down fingers and backup bar were coated with Rokide "Z" flame-spray coating applied to all surfaces in contact with the weld piece. Since the ceramic coatings are used primarily in compression, mechanical coating failures are not a problem, and the hardness of ceramics greatly reduces wear on these pieces. The main function of the coating arises from the thermal isolation of the holding devices from the weldpiece. Rokide "Z" is essentially a calcia-stabilized zirconia which possesses a thermal conductivity only about one one-hundredth that of high-conductivity metals. Now, the contact resistance is no longer the greatest thermal resistance in a series thermal conduction circuit as is the ceramic coating. Consequently, the variations in contact resistance are reduced by the larger thermal resistance of the coating. Effectively, the coating has separated the chilling effect from the positioning-and-holding action of the welding fixtures.

This new approach to the problem has been successfully used in the Saturn and Apollo weld tooling. In certain structures honeycomb facing sheets require a tolerance of ±0.005 inch and buckling cannot be tolerated. These difficult welds were successfully produced with the new tooling, whereas great difficulty had been previously experienced with similar type welds. Subsequent tests of welds produced with the copper type, chill hold-down bars gave strength values of 40,000 psi, while welds produced with coated tooling gave strengths of 60,000 psi.

For NASA applications this significant improvement in welding technology will allow the possible use of lighter spacecraft material or assure an increase in weld reliability. Further appreciable reduction in tooling costs were obtained by permitting less rigid tooling tolerances and using cheaper mild steel and aluminum in place of high strength, high conductivity copper tool materials.

THERMAL PROTECTION COATING FOR GATE VALVE EXPOSED TO ULTRA-HIGH TEMPERATURE HYPERVELOCITY AIR FLOW

A hypervelocity, high-temperature, airflow, experimental apparatus, constructed at the NASA Ames Research Center, required the development of a special gate valve. This valve was exposed to a 4,000 to 5,000° F temperature and high pressure air for 30 msec during operation. Figure 64 shows a view of the valve as currently constructed and gives an understanding of the operational mode of the gate mechanism.

Originally the valve consisted of a brass gate sliding over a stainless steel base. However, due to the extremes of air pressure and temperatures, the surfaces of the gate melted and subsequently welded to the steel base. Valves failed after a single closure. The original design was
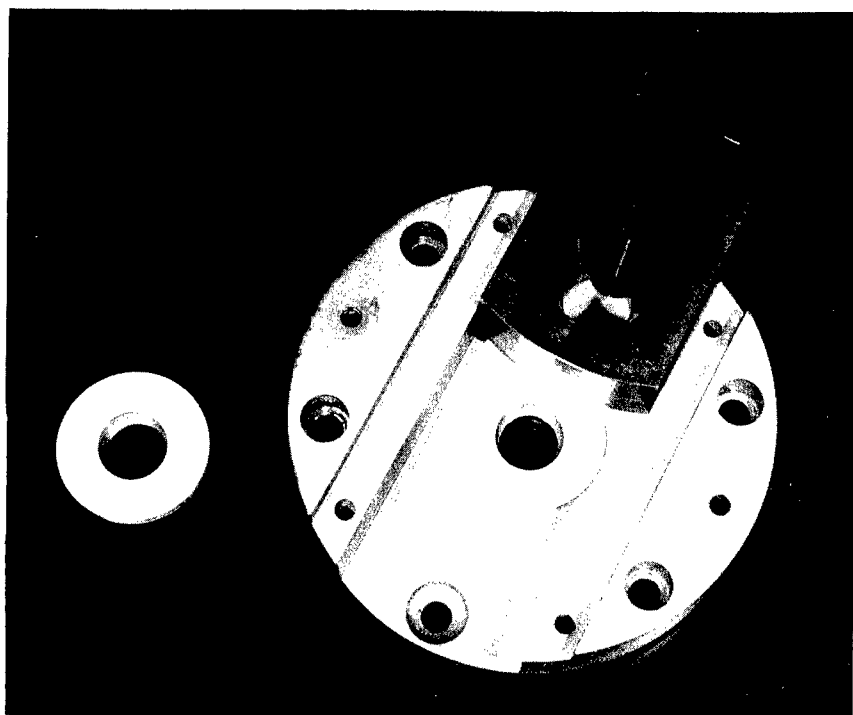
FIGURE 64.—View of gate valve used in high-temperature application with seat protected by thin layer of inorganic coating. Spare coated insert to side.

modified to make the gate and base from copper. The rationale for this change of material was the hope that the higher thermal diffusivity of copper would prevent the buildup of temperature at the material surface to prevent melting. This design was equally unsatisfactory and the valve welded shut after each operation.

The present valve design, which was developed by Ames' experimental craftsman Abe Brass, has operated successfully and consisted of a ceramic insulating coating applied to the bearing surfaces of renewable inserts. The ceramic oxide serves as a heat shield to the base metal and also becomes molten on the surfaces to serve as a high-temperature lubricant to reduce sliding friction during closure.

The specific technique found most suitable is to spray the valve base insert with an 8-mil-thick coating of aluminum oxide. Then, the coating is ground down to a 5-mil thickness. The thin coating is required to prevent cracking or chipping due to thermal shock. After prolonged usage the coating surface deteriorates primarily due to ablation. However, it is a reasonably simple and inexpensive operation to grind away the old coating and restore a new surface to the valve insert.

THERMAL PROTECTION COATING FOR LABORATORY FURNACE INDUCTION COIL

The use of induction heating for high-temperature, laboratory furnaces is currently widespread. Most apparatus consist of a fused silica, water-cooled, inert gas or vacuum chamber containing a susceptor surrounded by several radiation shields. Power is supplied to the susceptor by a current concentrator placed within the induction coil inside the furnace chamber. Usually induction coils are copper tubing energized by a high-frequency power supply. In the case of some high-temperature furnace systems large quantities of power are supplied, some of which radiate from the radiation shield back to the induction coil. In extreme cases the intensity of thermal radiation is sufficiently great so that even with cooling water flowing through the induction coil the surface of the copper melts and a hole develops.

Sikora (ref. 11) of the NASA Lewis Research Center experienced failures of this type several times and subsequently used a ceramic coating to provide thermal insulation which overcame the difficulty.

After the induction coil was formed, a "Rokide A" (aluminum oxide) coating was sprayed on the coil surface to provide both electrical and thermal insulation. Achieving a good bond proved difficult; however, by sand blasting the copper surface and following this with an acid pickling operation, usable adherence was obtained. This coating provides suitable thermal insulation because of the lower conductivity of the aluminum oxide as compared to the copper. Thus, while the outer
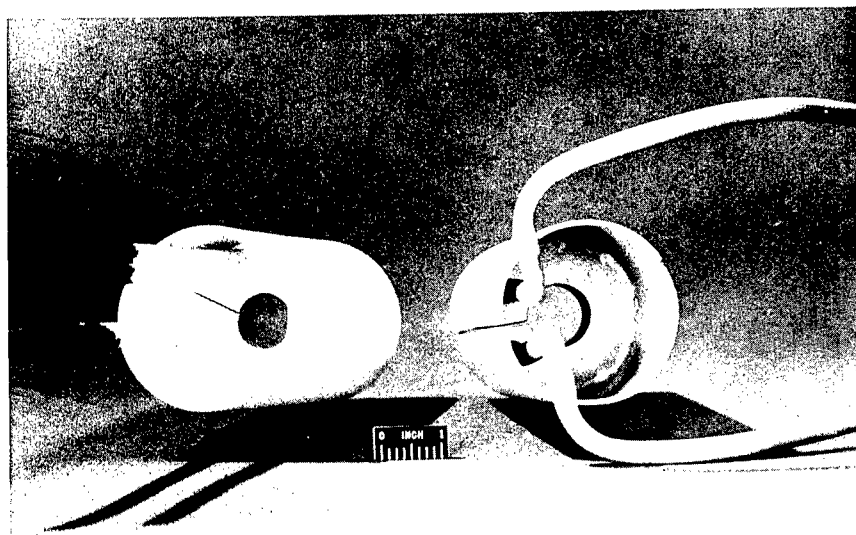
FIGURE 65.—Flame-sprayed aluminum oxide coated induction coil for high-temperature furnace.
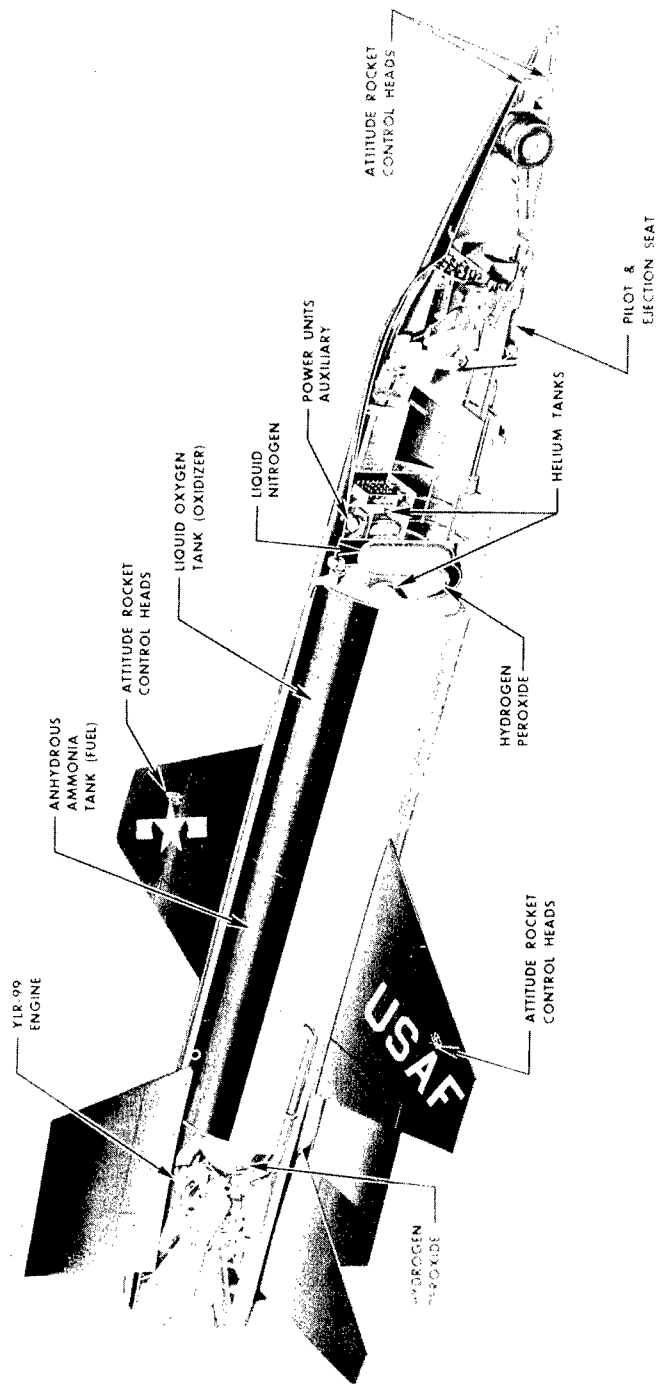
FIGURE 66.—Cutaway drawing of the X–15 fuselage.
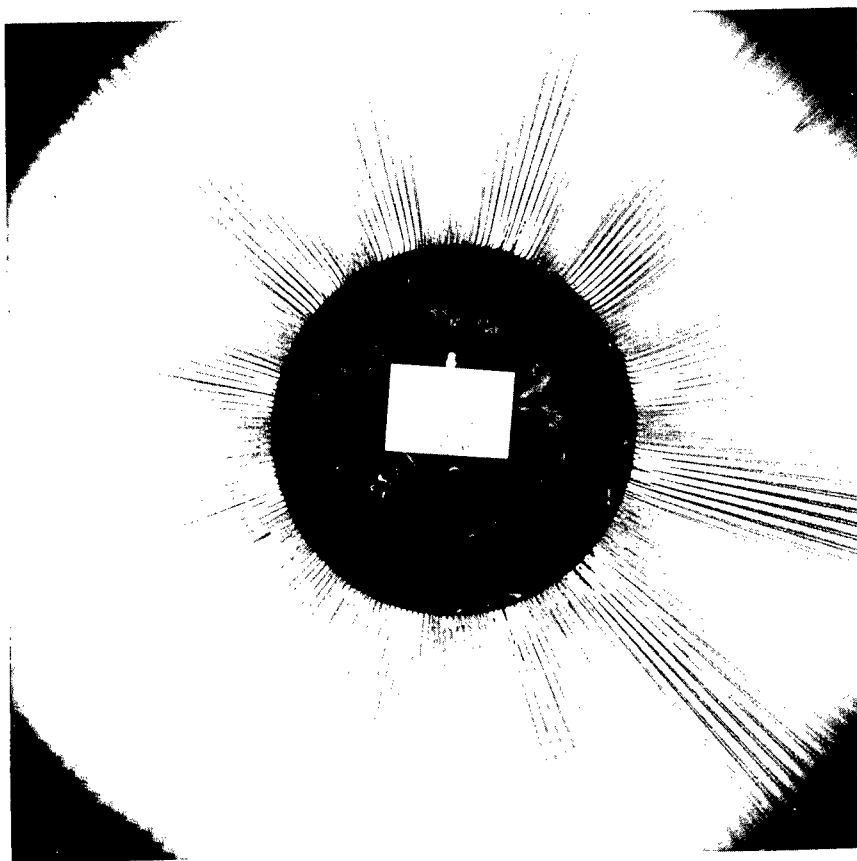
FIGURE 67.—Erosion of the thermal protective coating in the YLR–99 engine throat of the NASA X–15 research aircraft.

aluminum oxide surface reaches a significantly higher temperature during use, the copper interface temperature is reduced.   These coatings, which have performed satisfactorily for a period of two years, are shown in figure 65.

THERMAL PROTECTION OF THE NASA X-15 ROCKET ENGINE THRUST CHAMBER

Hjelm and Bornhorst (ref. 12) of the U.S. Air Force Materials Laboratory, Wright-Patterson Field have reported on investigations undertaken to develop suitable thermal protection coatings for the rocket engine and thrust chamber on the NASA X–15 aircraft.   The X–15 (fig. 66) is powered by an XLR 99 engine constructed by the Reaction Motors Division of the Thiokol Chemical Corp.   The XLR 99 engine is fueled with liquid oxygen and anhydrous ammonia.   The combustion chamber
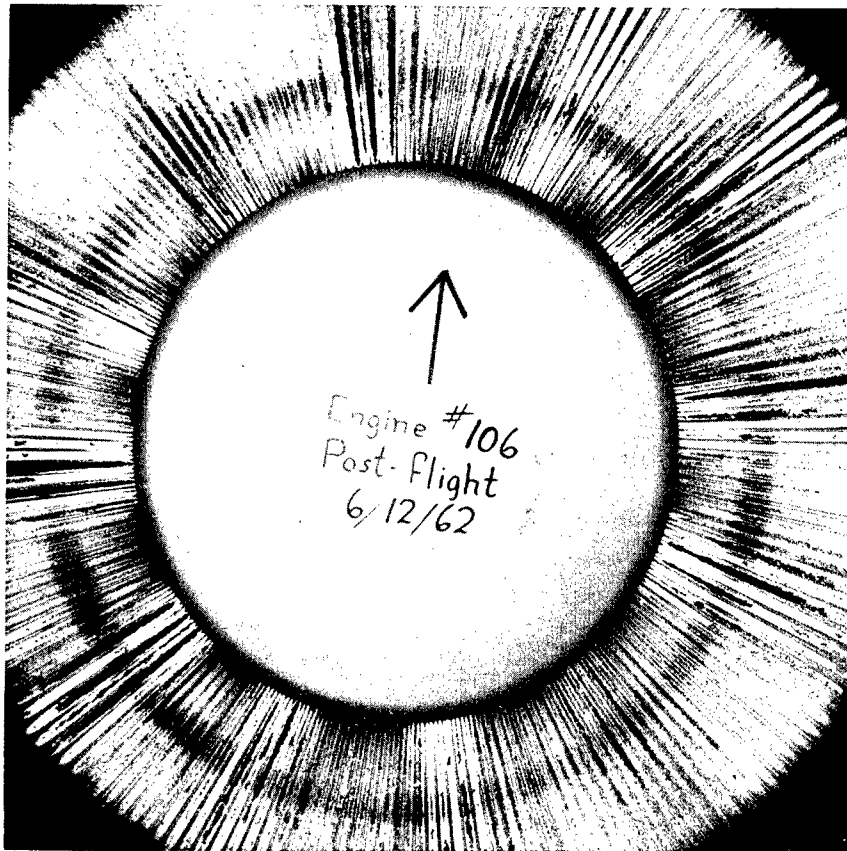
FIGURE 68.—Detailed view of X–15 engine thermal protection coating erosion.

is constructed of a brazed assembly of 347 stainless steel tubes. The liquid fuel regeneratively cools the engine by passing through the tubes prior to combustion. In order to reduce the cooling load, a thermal insulating, 10-mil-thick coating of stabilized zirconia, Norton Co. "Rokide Z", is applied over a 5-mil-thick nichrome undercoat.

In service, this coating spalled from the surface (figs. 67 and 68) due to a combination of vibration during operation and thermal shock upon starting the engine. Coating loss just behind the throat area can be clearly seen in figure 68. It is apparent that a lack of coating-substrate bond is responsible for the failure. When the coating is detached, the heat flux to the liquid ammonia is sufficiently great to cause film boiling. The ammonia gas reacts with the stainless steel to form nitrides and embrittle the metal. Furthermore, the exterior of the stainless surface becomes sufficiently heated so that vaporizing and melting reduce the

tubing wall thickness; consequently a leak develops and the engine is unserviceable.

The approach to solving this problem was to develop a new gradated coating system which in effect eliminates the coating-substrate interface. Coatings of this type were produced by the Plasmakote Corp. by plasma-spraying mixed powders and gradually changing the ratio of metal and ceramic powders. Zirconia was retained as the ceramic, while nichrome, molybdenum and tungsten metals were used. The University of Dayton developed realistic evaluation techniques for the test screening samples. Thermal shock effects were determined by using a 3- by 8-inch section of the actual chamber and water cooling it while a 50-kw nitrogen-stabilized arc-plasma was used to heat the plate through ten cycles, with nine increases in heat flux. Water-cooled and coated tubes were used in the initial shock tests while simultaneous heat transfer measurements were made by using the tube as a calorimeter.

The three coatings selected for testing are detailed in table 23. The only difference in the gradated coatings is the undercoat primer used over the stainless tubes. Coating (A) used a 3-mil-thick nichrome primer and coating (B) a 3-mil-thick molybdenum layer. Laboratory tests of the three coatings are given in figure 69 as a probability of failure versus the total cycles to failure relationship. It is obvious that coating (B) is markedly superior to coatings (A) and "Rokide Z".

The engine test program was undertaken using coating (B), applied by the NASA pantograph spraying-control system which produces uniform coatings over the internal surface of the combustion chamber. (See Methods of Applying Coatings to Substrates.) Results of the test program are encouraging but are not yet completely definitive. The first test series ran a new "Rokide Z" coating on an old chamber as a basis of comparison with the gradated coating applied to an old leaking chamber which had the leaks welded shut. At the end of the seventh run and a total firing time of 5½ min, a total of 25 sq in of "Rokide Z" had been lost. The gradated coatings fired six times over 5¾ min showed a loss of 3 sq in of coating all in areas where the repair welds had broken. Slight erosion was visible in other areas, and chipping of the coating occurred upstream of the throat. The zirconia darkened during the first test run; and at first this was thought to be due to nichrome diffusion through the coating. However, when metallographic examination showed that this had not occurred, it was concluded that oxygen-defect promotion in the zirconia was the probable cause of the blackening observed. There was no indication that the darkening adversely affected the coating performance, though it must have increased the surface emittance and thereby increased the heat transfer through the coating.

TABLE 23.—*Thickness and Identification of Coating Systems*

Coating designation	Primer	Gradation 1	Gradation 2	Gradation 3	Insulating layer
Rokide Z	0.004-inch Nichrome				0.010-inch Rokide Z (ZrO_2)
Coating A (Plasmakote)	0.003-inch Nichrome	0.003-inch 70% Nichrome 30% ZrO_2	0.003-inch 30% Nichrome 70% ZrO_2	0.003-inch 10% Nichrome 90% ZrO_2	0.004-inch ZrO_2
Coating B (Plasmakote)	0.003-inch Molybdenum	0.003-inch 70% Nichrome 30% ZrO_2	0.003-inch 30% Nichrome 70% ZrO_2	0.003-inch 10% Nichrome 90% ZrO_2	0.004-inch ZrO_2
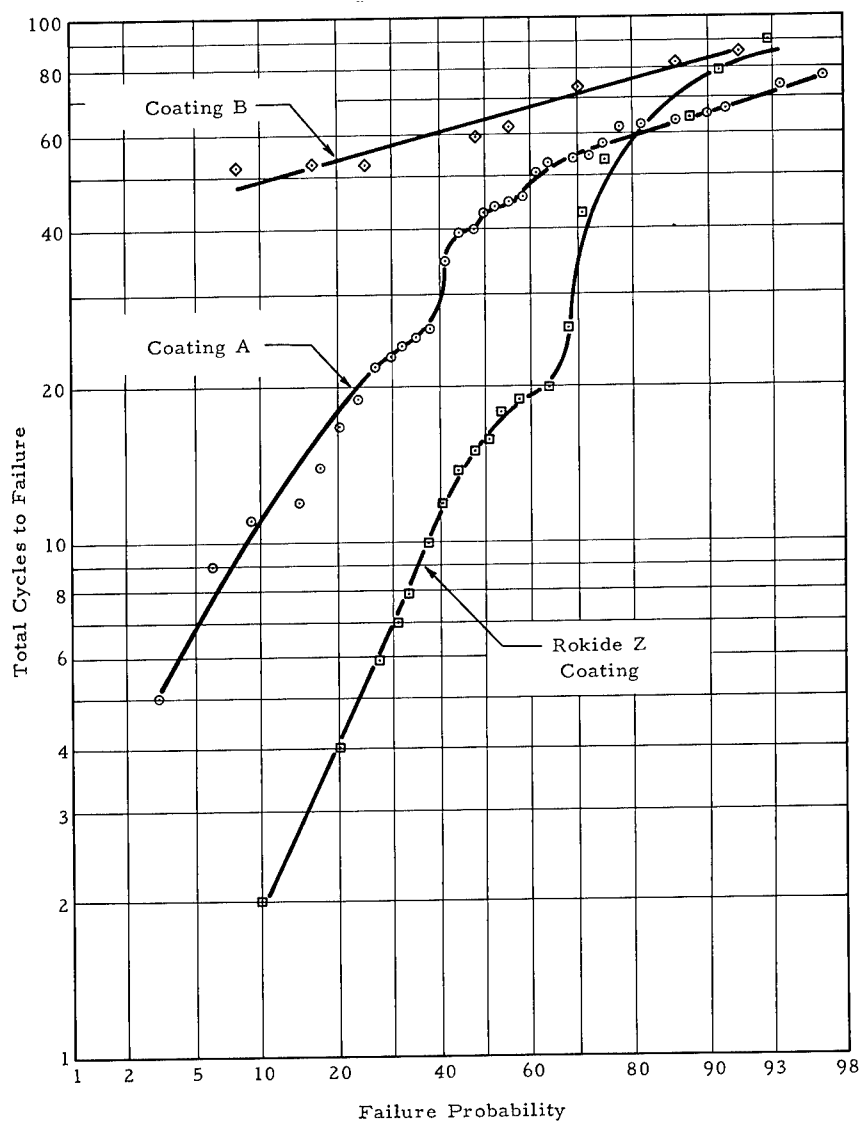
FIGURE 69.—Probability of thermal-shock failure.

Additional development work is being carried on with molybdenum-zirconia and tungsten-zirconia graded coatings and titanium nitride and zirconium diboride cover coats. This work includes additional attention in attempting to improve the "Rokide Z" adherence. Improvements in this area are being made by active work which is being aggressively pursued. Further developments are desirable from an economic standpoint, even though the engine operates satisfactorily. The X–15 had

TABLE 24.—*Future of Coating Development*

Engine Test Results

Good

Bad

Refine Current Coatings

Refine First Coatings

New Lab Test

Old Lab Test

Best Coating

Best Coating

Engine Test

Operational Program
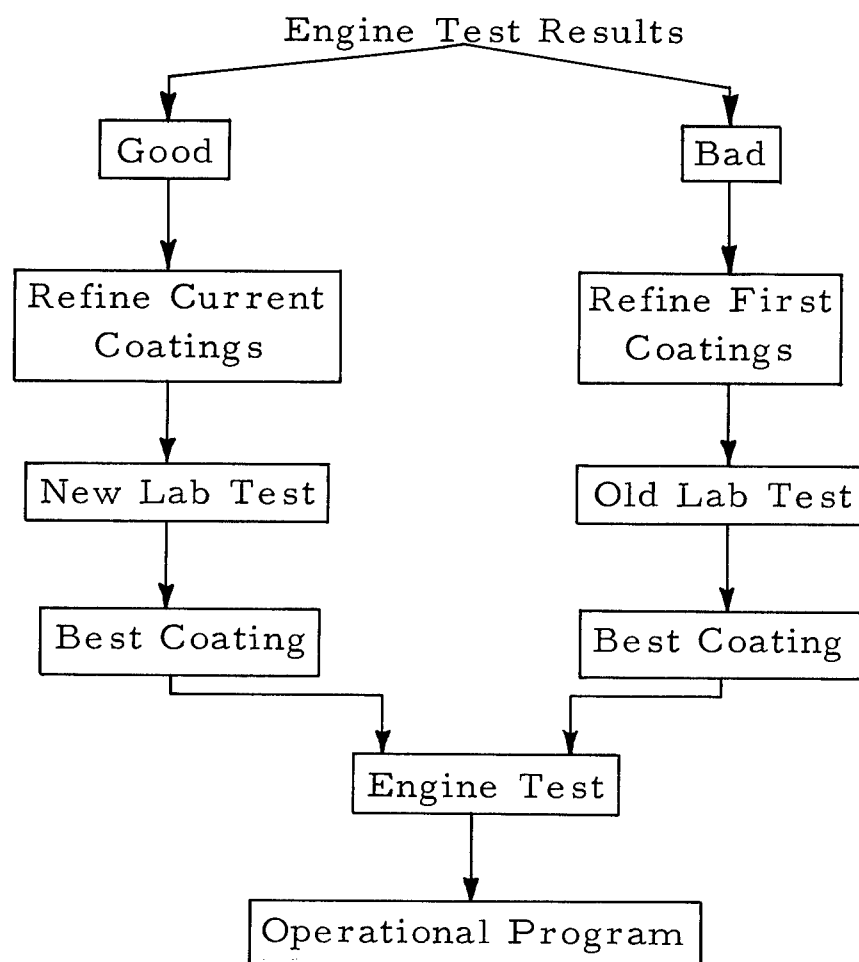
successfully achieved 100 flights as of January 28, 1964, and has proven to be a useful research aircraft (ref. 13). Future coating development plans are shown in table 24.

COMMERCIAL IMPLICATIONS

GENERAL TECHNOLOGY

The development of thermal protection systems has involved a sizable investment, primarily for defense purposes, and only secondarily for NASA purposes. The major commercial contribution of these programs

is not identified as a product, but as a growing awareness by researchers and designers of the importance and significance of thermal parameters in design. Awareness brings new patterns of thought and new analytical techniques which become an important part of our technical heritage. The specific applications are not now obvious, except for the more trivial cases, but as the commercial technology develops in its utilization of higher power densities the relevance of what now seems hopelessly advanced technology will become useful.

For example, the development of thermal insulation coatings for protection of aerodynamically heated structures or rocket engines are directly applicable to advanced high-temperature, chemical, processing equipment. The fixation of nitrogen is typical of the processes which become more efficient with increased temperature and pressure. The generation of power from plasmas with magnetohydrodynamic generators will require high-temperature insulations to improve thermal efficiencies. Methods developed in producing thermal insulations will be generally applicable to the production of thermal insulators for fuel cells, or perhaps for electrical conductors which conduct by specific charge and mass transport mechanisms. In addition to these broad possibilities we want to list specific developments that are currently occurring, and offer suggestions, as to potential coatings applications, for consideration by those technical people who have specific cost data at hand for full commercial evaluation.

FIBROUS INSULATIONS

The following representative commercial organizations are currently producing high-temperature fibrous insulations for the aerospace and commercial applications.

1. Carborundum Company
   Ceramic Fiber Plant
   Niagara Falls, New York
   "Fiberfrax"

2. E. I. du Pont de Nemours, Inc.
   Wilmington, Delaware
   "Tipersul"

3. Johns-Manville
   Manville, New Jersey
   "Min-K"

4. H. I. Thompson Fiber Glass Co.
   1600 West 135th Street
   Gardena, California
   "Refrasil"

Table 25 is taken from the "Fiberfrax" applications information supplied by the Carborundum Company which indicates typical applica-

tions of the proprietary product. We do not intend to imply that NASA directly supported the development of these materials or products. However, alert companies have supplied the aerospace requirements and by satisfying rigid performance specifications have improved their product; this improvement is a tribute to these private organizations and is being made available directly to the commercial economy. This situation represents one level of Government-industry cooperation.

TABLE 25.—*Suggested Applications for "Fiberfrax"**

Furnaces _____	High-temperature furnace insulation and expansion-joint packing.
	Combusion chamber liners in domestic heating units.
	Hydrogn atmosphere furnace linings.
	Insulation for furnace shafts and refractory rollers.
Metal Working ___	Encapsulation of rare metals in vacuum annealing.
	Casket material in vacuum casting of alloy-steel ingots.
	Hot tops for metal ingot molds.
	Coatings to decrease oxidation rate of graphite or metals.
	Liners for ladles, troughs, spouts and molds in nonferrous metal processing.
	Molten aluminum distributor pan linings.
Glass and Ceramics _____	Lehr roll covers in glass annealing and rolling.
	Cushioning media in processing of ceramics.
	Ceramic kiln linings for faster firing cycles.
Space Age _____	Acoustical and thermal insulation for jet engine test cells.
	Component for ablation nose cone materials and missile antenna windows.
	Liners for hypersonic wind tunnels.
	Insulation of fuel cells and firewalls in jet aircraft.
Brazing _____	Cloth blankets for electric-blanket brazing.
	Brazing and heat treating process separators.
	Mechanical cushioning and thermal insulation in metallic honeycomb brazing.
Electrical _____	Braided covering for high-temperatur wire and cable.
	Electrical insulators in circuit breakers.
Filters _____	Filters for high-temperature gases.
	Filters for removal of radioactive particles from reactor exhaust gases.
Other _____	Braker lining additives.
	Superheater section insulating walls in marine boilers.
	Heat-resistant clothing and flame curtains.
	Portable flange covers for naval vessels.
	Insulation of ducts and pressure vessels permitting use of low-cost steel structures.
	High-temperature steam turbine covers.

* Fiberfrax—Trade Name of Carborundum Company. Ceramic Fiber Plant, P. O. Box 337, Niagera Falls, New York

UNFIRED FOAM INSULATIONS

The commercial implications of the NASA-developed, low-temperature curing aluminum phosphate insulation are obscure due to the lack of complete technical information. However, the following uses were suggested by Eubanks and appear reasonable from a technical point of view.

1. Building materials
2. Furnace and stove insulation
3. Heat resistant potting compound for electronic modules
4. Steam pipe insulation
5. Fireproof acoustic tiles
6. Thermally insulated containers
7. Fire protection barriers
8. Thermal and optical reflectors

The largest usage for this material may probably be for insulating industrial ovens and furnaces. Phosphate mortars and cements are not new for these applications and have been discussed by Kingery (ref. 14); Gitzen, Hart, and McZura (ref. 15), and Gilham-Dayton (ref. 16). A complete literature survey is available from the studies of Ott and Allen (ref. 17). Currently the major refractory insulating materials are insulating firebrick which are available in standard sizes (9 by $4\frac{1}{2}$ by $2\frac{1}{2}$ inches) and special shapes for specified temperature service up to 3,000° F. Although less used, castable and insulating coatings are supplied by most major refractories companies. Most current castable insulations are based on silicate binders.

Aluminum phosphate insulations have two major technical advantages over silicate type materials: (1) high strength at all temperatures, and; (2) greater refractoriness. Silicates have good strengths at room temperature due to water-of-hydration type bonding. With increasing temperature this hydration water is driven off and the bond strength decreases starting at about 1,200° F. Above 1,600° F a glassy bond forms and the strength rises back to its original value. In a cast-insulating wall with a 2,500° F hot face temperature and a 400° F outer surface temperature there will be a zone of weakness within the insulating layer corresponding to the temperature range 1,200° F to 1,600° F. Secondly, because phosphate cements are more refractory than most silicates, they have an advantage in higher temperature applications.

Offsetting these advantages of phosphates, to an indeterminate extent, is the corrosive nature of the cement and its greater expense. High-quality, high-heat-duty, silicate castables sell for about $200/ton. The estimated selling cost of aluminum phosphate mortars, cements, and castable insulations is approximately $1,000/ton. However, with the greater service life and higher temperature capabilities and low-temperature curing properties, phosphates can still be competitive for many applications. A full cost analysis relating to insulating firebrick shows a sizeable placement cost which is not incurred when forming foamed materials inside cheap shaping forms.

The marketing of foamed aluminum phosphate materials requires the

development of specialized mixing and placement equipment. It is not clear that present refractories producers would want to market this apparatus since it is possible that the user would buy the raw materials directly from primary producers. Thus the refractory producer might lose a current market as regards the sale of refractories.

It is estimated that foamed aluminum phosphate insulating materials have a number of commercial applications, particularly within the field of refractory applications.

HIGH-TEMPERATURE INSULATING FOAMS

The Ipsen Industries, Inc., Rockford, Illinois, currently is producing two materials of a type similar to that being developed at the National Beryllia Corp. These materials differ in one important detail; the Ipsen insulating material has continuous pores, and the National Beryllia material has primarily closed pores. This difference is important for some applications; at times one material is favored over the other and vice versa. In general both of these materials are useful for high-temperature service over and above the range served by more conventional alumino silicate-refractories.

WELDING TOOLING

This novel application is a contribution to welding technology. For some metals the limitation of the heat-affected zone by local "chilling" is a necessity and the application of insulating coatings to holding equipment will reduce weld uniformity and strength. However, for many materials which are less sensitive to the development of a heat-affected zone this will be a useful innovation. The application of this development to specific welding problems will require competent professional metallurgical skill.

THERMAL PROTECTION OF GATE VALVE

No commercial valve applications are known having such rigorous operational requirements. However, the increasing use of higher and higher temperatures in chemical processing and power production equipment may require the use of inorganic coatings or components.

The commercial implications of rocket linings and protection coatings for laboratory induction coils is probably not great. However, these specialized uses represent the kind of applications which will probably develop in the future. As problems of thermal protection arise here and there throughout our whole commercial economy, coatings for thermal protection will be known, available, and used. Specific usage is not predictable.

Methods of Applying Coatings to Substrates

GENERAL TECHNOLOGY

The combination of two materials, as a coating and substrate that results in a materials system possessing useful (and frequently superior) properties, has almost unlimited potential. While the basic optical, thermal, mechanical, electrical, and magnetic properties are not completely known, enough information is available so that it is possible to choose from among the known ceramics, metals, intermetallics, and interstitial compounds one or more materials for a particular coating application. However, the difficulty usually arises in applying the chosen coating to the substrate. It is not only a question of bringing two materials together physically, but also of achieving some degree of bonding.

Bonding or adherence of coatings to substrate has commonly been produced by bringing two materials together and applying heat and pressure. Bonding was achieved by the mutual wetting of surfaces or the interdiffusion of materials at the interface. Older coatings methods are being supplemented, or displaced by new procedures. Even so, the demand for new techniques which apply coatings in a predetermined, controlled, and reproducible manner is very large. In many cases of acute need the factor which limits the advance of coating technology is the need for new coating methods. A similar need exists to understand more fully, particularly at the fundamental level, the factors governing older processes. Too few good parametric studies have been made of coating process variables. The number of sound statistically-designed process investigations has been disturbingly small. Moreover, fundamental scientific investigations of surface properties, interlayer bonding, and structures of coating substrate interfaces have been much too few.

On one hand we see the construction and operation of larger and more elaborate coating apparatus and on the other an appalling lack of understanding of the principles which make these devices operate. While the NASA expenditures for coating applications are small with respect to the total efforts expended in both our aerospace and commercial economy, the NASA work has been important and in many cases particularly

significant.   However, the demands for coatings and more specifically for coating methods are growing at a faster rate than progress is being made in developing newer methods or refining older methods.

Methods for applying coatings can best be categorized in terms of the size of the particles which are being used to produce the coating structure. These are: (1) atomic species; (2) particle material; and, (3) sheet material.   On this basis, the following categories provide a reasonable framework for discussing coating methods.

1. Atomic Species Processes
      Vacuum Deposition
      Cathode Sputtering
      Vapor Deposition
          Pack Cementation
          Vapor Phase
      Electrodeposition
          Fused Salts
          Molten Metals
          Aqueous Solutions
          Organic Solutions
2. Particulate Material Processes
      High-Temperature Coatings
          Flame Spraying
          Arc-Plasma Spraying
      Enamelling
      Painting
      Trowelling
      Electrophoresis
3. Sheet Material Processes
      Laminating
      Cladding

COATING WITH HIGH-TEMPERATURE PARTICLES
PARTICLE-PLASMA INTERACTIONS AND THEIR RELATIONSHIP TO COATING STRUCTURE AND ADHERENCE

A strong and growing aerospace coating technology exists to develop and manufacture apparatus for coating hardware items using high-temperature particle coating processes.   In addition, numerous firms are developing and perfecting coating materials and techniques to achieve higher performance coatings.   NASA has utilized commercially-developed apparatus for its coating requirements at several research centers as shown in figures 70 through 72.   NASA research work in this field has consisted of a small effort (less than a 2-man-year).   However, the results have been particularly significant since they are directed toward
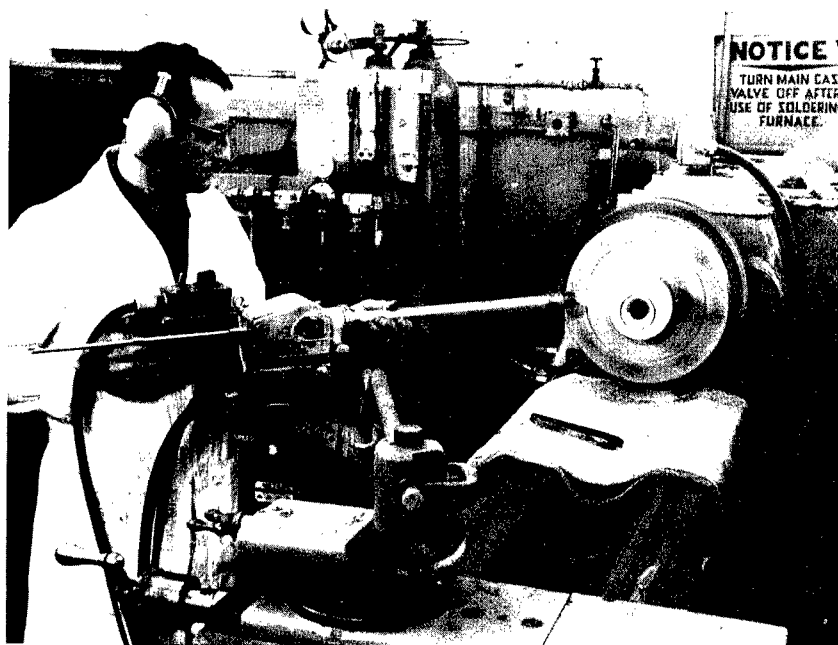
FIGURE 70.—View of equipment used for applying inorganic coatings (aluminum oxide) to cylindrical shapes.

understanding the greatest deficiency of hot-sprayed coating; namely, the lack of adherence.

Grisaffe and Spitzig (ref. 1) (NASA Lewis Research Center) have, on

TABLE 26.—*The Adherence of a Hot-Sprayed Coating Must Depend upon the Process Parameters which Grisaffe and Spitzig Listed as Follows*

1. Particle Factors
    a. Temperature
    b. Velocity
    c. Mass
    d. Density
    e. Thermal Conductivity
    f. Specific Heat
    g. Thermal Expansion
    h. Dynamic Viscosity
    i. Surface Tension
2. Substrate Factors
    a. Temperature
    b. Hardness
    c. Surface Finish
    d. Thermal Conductivity
    e. Specific Heat
    f. Thermal Expansion
3. Plasma Factors
    a. Temperature
    b. Velocity
    c. Composition

FIGURE 71.—Application of inorganic material to representative pieces.

a part-time basis, directed their investigations toward understanding the
particle-plasma interactions in terms of thermal and kinetic energy
exchange and elucidating the arc-plasma parameters (table 26) and their
effect on the initial individual particle-substrate bond.   Former studies
were primarily concerned with coating microstructure development
rather than adherence.
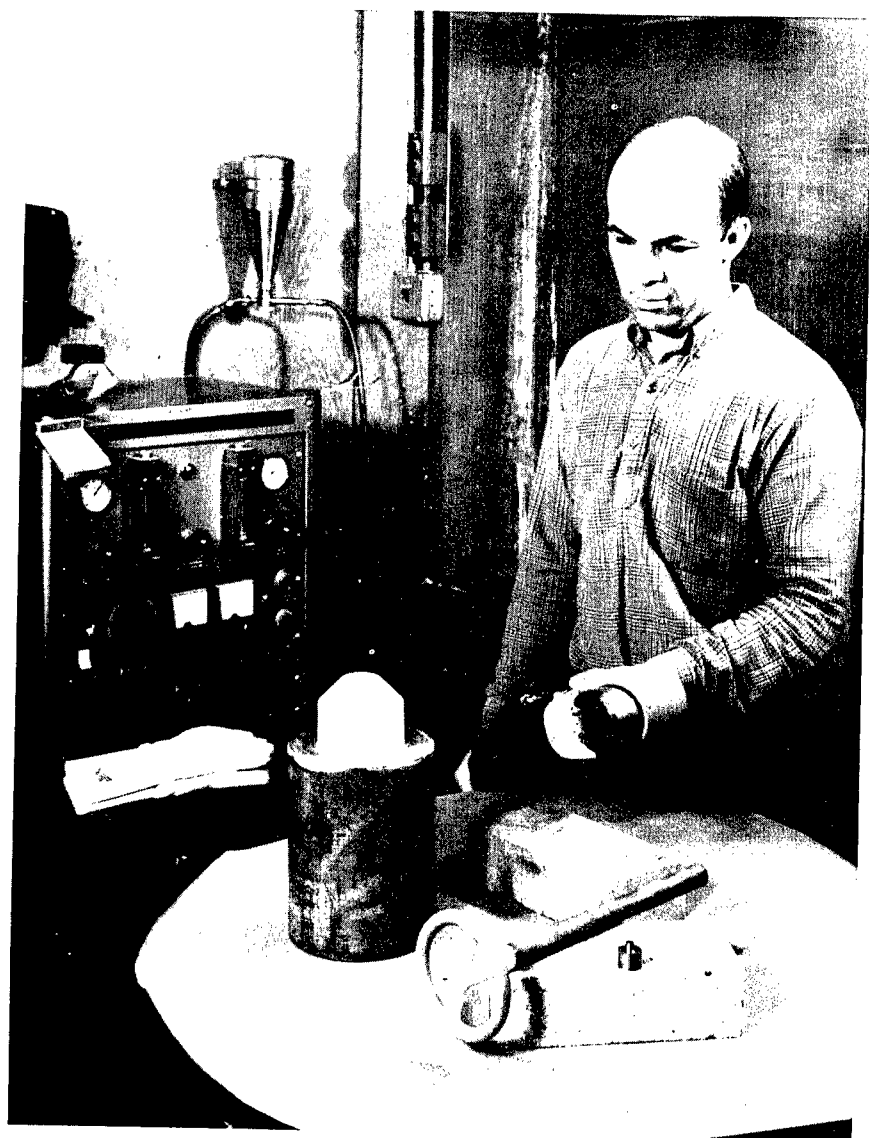
FIGURE 72.—View of equipment used to apply inorganic materials at the Ames
Research Center.   Representative examples of work are included.

Theories of ceramic-to-metal bonding have been of concern to the
porcelain enamel industry for years and a short review of this information
is in order.   The classic treatment by King, Tripp, and Duckworth
(ref. 2) reviewed the literature, conducted experimental investigations and
concluded that both mechanical-interlocking and metal-to-metal bonds
between the atoms in the base metal and similar ionic species in the glass

phase were required for good adherence. They extended the prior studies of Richmond, Moore, Kirkpatrick, and Harrison (ref. 3) of the National Bureau of Standards, which clearly identified that a mechanical-interlocking of porcelain enamel on steel correlated with interfacial roughness. The most important correlation was with undercut areas, "anchor points" rather than surface area. Sandblasting or mechanical surface roughening prior to firing porcelain-enamel was of little significance in increasing adherence. It was therefore concluded that significant enamel-substrate interactions generated the significant anchor points. Factors other than surface roughness influenced adherence but these remained unidentified. Thus at least two types of adherence factors, mechanical-interlocking and chemical-bonding, play important but not clearly defined roles for porcelain-enamel metal systems.

Fundamental understanding of the bonding of high-temperature particle coating was really nonexistent. The only practical knowledge was that sandblasting usually, but not always, improved coating adherence, probably by increasing layer-substrate interlocking. Therefore, to study and elucidate other bonding mechanisms, only metallurgically-polished metals and polished-glass substrates free of initial surface roughness were used by Grisaffe and Spitzig (ref. 1). Before actual coating experiments were conducted, analytical and experimental studies of particle-plasma energy interactions were made.

The heat transfer from plasma to particle was derived assuming: (1) plasma stream temperature is constant along its length; (2) particles are homogeneous, isotropic, and spherical; (3) thermal conductivity, specific heat, and density of particles are temperature-independent; (4) heat of fusion is zero; and, (5) liquid properties are the same as those of the solid. The equation for heat transfer for a sphere initially at zero temperature, which is instantaneously increased to a constant surface temperature (T_s), is as follows:

$$\frac{T}{T_s} = \left[1 + \frac{2R}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \sin\left(\frac{n\pi r}{R}\right) \exp - \left(\frac{\alpha t n^2 \pi^2}{R^2}\right) \right]$$

where:

T = temperature of particle at radius (r)
T_s = surface temperature of particle
R = radius of particle
r = distance from center to point in the particle
n = integer
α = thermal diffusivity $(k/c, \rho)$
t = time of residence of particle in plasma stream
k = thermal conductivity
c = specific heat
ρ = density

The heat transfer to zirconia, chosen because of its low conductivity, high density, and high melting point, should make it one of the most difficult materials to melt.   The material parameter $kt/C\rho R^2$ was calculated assuming the following values:

k = 0.75 Btu/hr, ft, °F
C = 0.170 Btu/lb, °F
ρ = 374 lb/cu ft
R = 30μ

Experimentally, it was determined that the average particle velocity for zirconia is 430 ft/sec over a 3-inch nozzle-to-work distance.   The residence time is:

$$t = \frac{0.25 \text{ ft}}{430 \text{ ft/sec}} = 0.000582 \text{ sec}$$

Therefore, $kt/C\rho R^2$ is equal to 0.20 in this case.   The ratio of temperature at any radius to the surface temperature for 60μ and 100μ particle sizes of zirconia, and 100μ tungsten particles is given in figure 73.   This plot suggests that these particles approach generally within 80 to 100 percent of their surface temperature within their time of flight from the nozzle to the work.   Residence time within the arc-plasma chamber would increase the true residence time to some extent.   Even if particles are not completely molten, their temperatures are near enough to the melting point to permit deformation under low stress levels.

All experiments were performed with a rigidly-mounted Thermal Dynamics F–40 arc-plasma spray unit used under the following conditions:

Spray nozzle I.D.	7/32 inch
Current	450 amp
Voltage	60 v
Plasma N_2 flow	80 standard cu ft/hr
Plasma H_2 flow	10 standard cu ft/hr
Carrier N_2	10 standard cu ft/hr
Continental hopper setting	11.9

Zirconia powder, comprising angularly-shaped particles of 44 to 62μ diameter, was used.   Tungsten powders, 30 to 62μ diameter, appeared to be composed of sintered chains.   Both materials, examined after passing through the plasma, assumed a more nearly spherical shape.

Spraying in air was accomplished by drawing the sample through the arc stream at a 1 ft/sec velocity.   This procedure permitted metallographic examination of individual impacted particles.   Nitrogen spraying was carried out in a water-cooled spray chamber evacuated to a total pressure of 20μ and backfilled with high-purity dry nitrogen.

The average particle velocity of tungsten decreased from 250 to 150
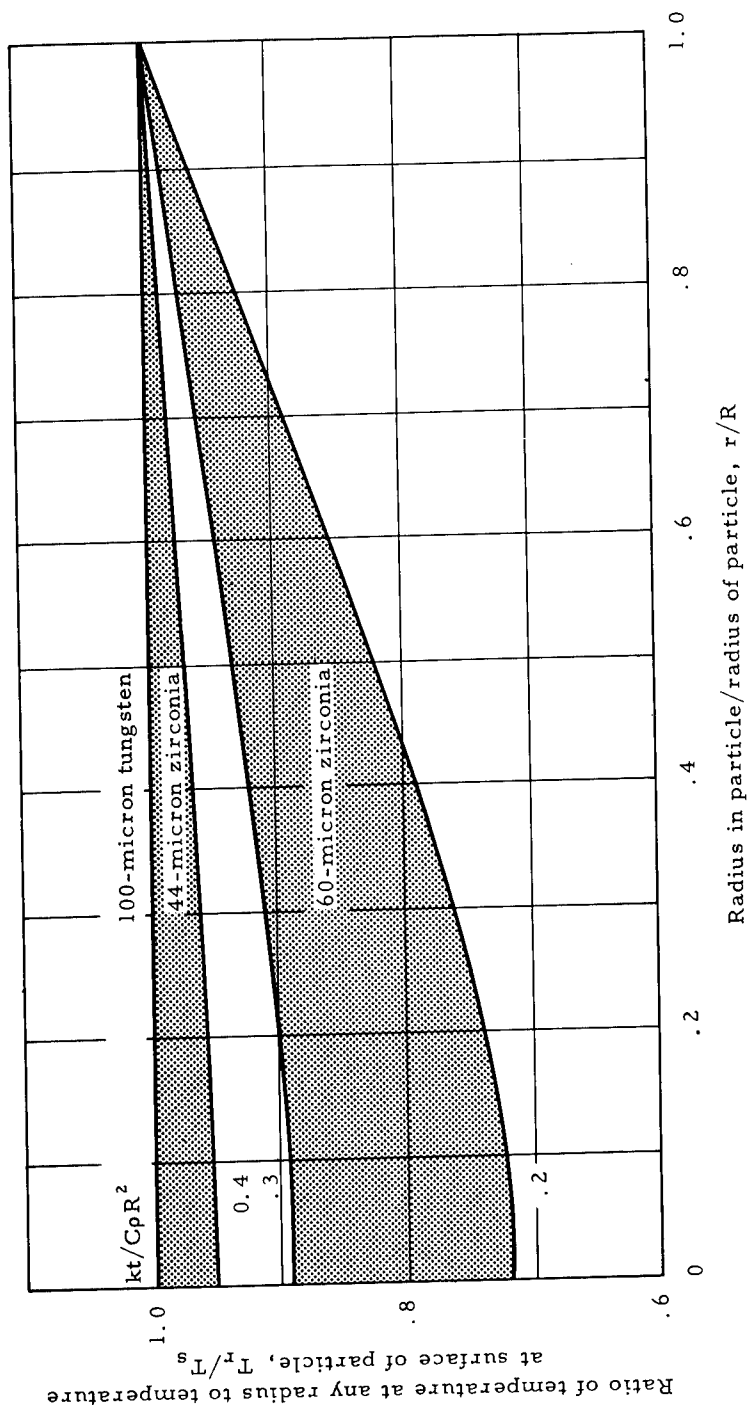
FIGURE 73.—Temperature distribution of some radius r within a sphere of radius R. Thermal conductivity, k; residence time, t; specific heat, C; density, p.
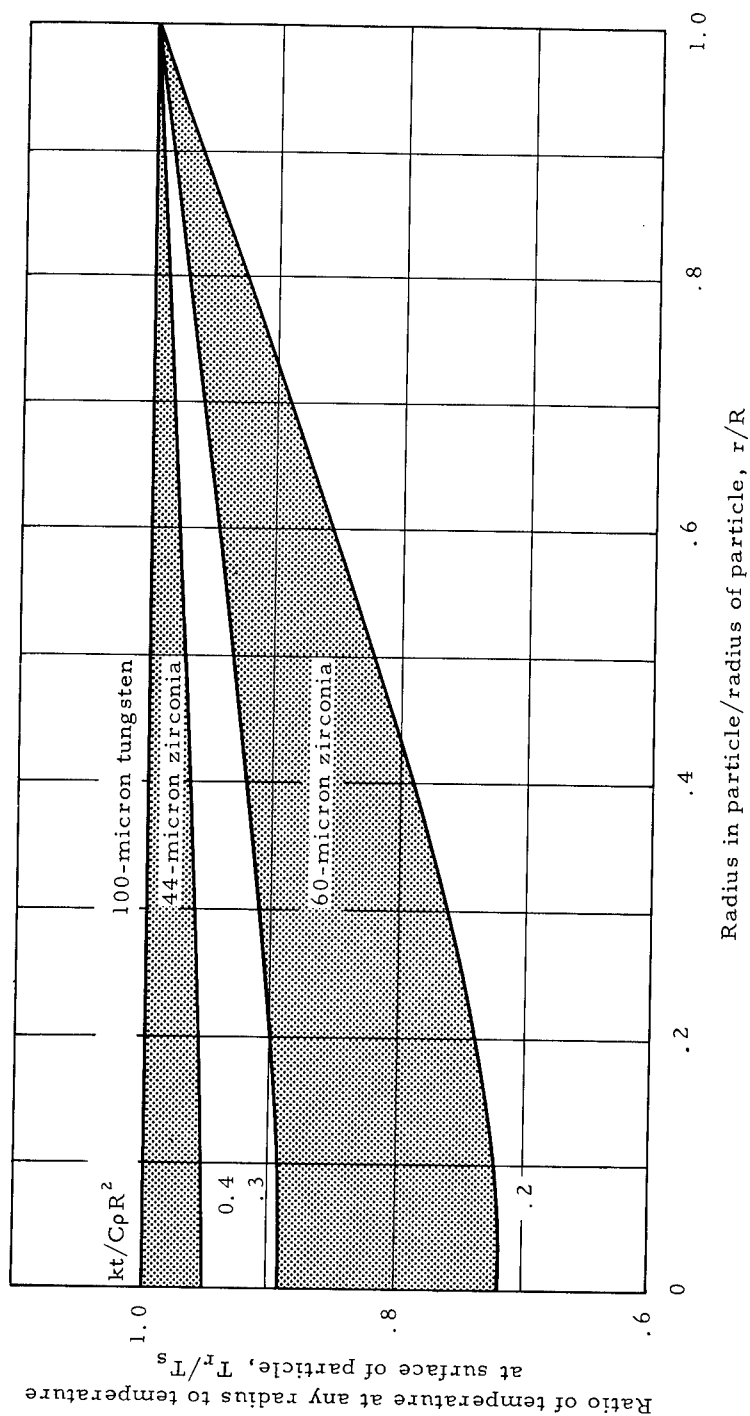
FIGURE 74.—Variation of average particle velocity with torch-to-substrate distance.

ft/sec at 3 and 11 inches from the plasma nozzle (fig. 74). The velocities were reasonably constant over the distances of 3 to 5 inches. Zirconia particles maintained a constant average velocity of 430 ft/sec which decreased to 310 ft/sec at 11 inches. Although the tungsten particle attained a lower velocity than zirconia, the lower density of zirconia resulted in the kinetic energy of both particles being approximately equal.

Based on measurements of particle velocity obtained by a rotating disk method, the kinetic energy of zirconia was calculated to be equal to $270 \times 10^6 \ d^3$ g/cm/sec^2, where (d) is the particle diameter in microns. For a 60μ particle the total kinetic energy is 58.4 dynes/cm.

TEMPERATURE MEASUREMENTS

Platinum-platinum-13 percent rhodium thermocouples are formed with a disk-shaped bead 10 mils thick and $\frac{1}{8}$-inch diameter to provide a large, low-heat capacity junction. A recorder with a millisecond response was used for temperature monitoring. Temperature measurements with and without particles in the stream were determined at 4 to 10 inches from the torch nozzle. The measured temperature reached equilibrium within $\frac{1}{2}$ sec. At 10 inches distance, the plasma temperature varied from 800 to 1,100° F, and was approximately 100° F higher when particles were introduced. At a 4-inch distance plasma temperatures ranged from 2,100 to 2,600° F and increased to 2,900° F when particles were sprayed.
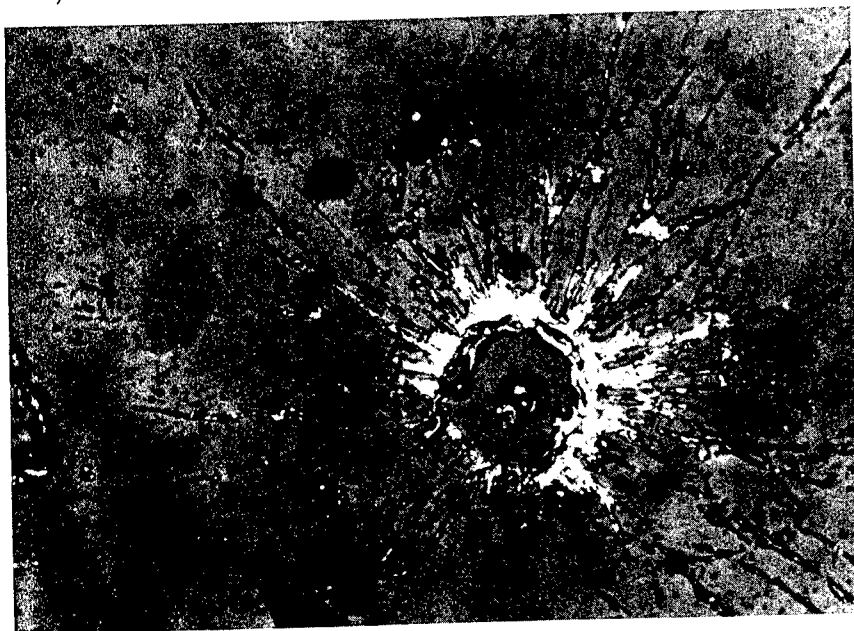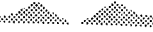
FIGURE 75.—Zirconia particles on glass substrate. Torch-to-substrate distance, 4 inches. X167.5.

TABLE 27.—*Particle Velocities, Temperatures, and Cross Sections of Zirconia Particles Sprayed on Glass*

Spray distance, in.	Average particle velocity, ft/sec	Approximate particle temperature, °F	Schematic average particle cross section	Remarks
3	425	3300		Particle splashed away from center and developed a rather high circumferential rim from which stringers proceed outward. No material at center of impact.
4	430	2800		Small amount of material remains at center of impact, and ridge is separated from it by region of no material. Stringers still proceed radially outward, but ridge is on inside.
5	430	2300		Ridge is on inside, but stringer length and number have decreased markedly.
6	385	2000		Center hole is much smaller, the ridge much heavier, and the few stringers much shorter.
7	350	1800		The ridge remains, but no central hole exists. Stringers have degenerated into surface discontinuities.
8	330	1500		Particle is a distorted disk. A few flow lines can be seen.
9	320	1400		Almost no deformation occurred.

Optical-measurements of zirconia particles in the gas stream indicated temperatures approximately 800° F higher at the same distances.   Since heat transfer depends to a major extent upon the optical properties of the thermocouple material, the surface temperature methods are subject to large errors.   Also the Shawmeter optical device used a two-color system for temperature measurement and small differences in emissivity at the two wavelengths cause large errors in temperature measurement. For these reasons the temperature measurements made must be viewed critically.

The microscopic investigation of zirconia and tungsten particles impacting on glass, stainless steel, tungsten and copper at various nozzle-
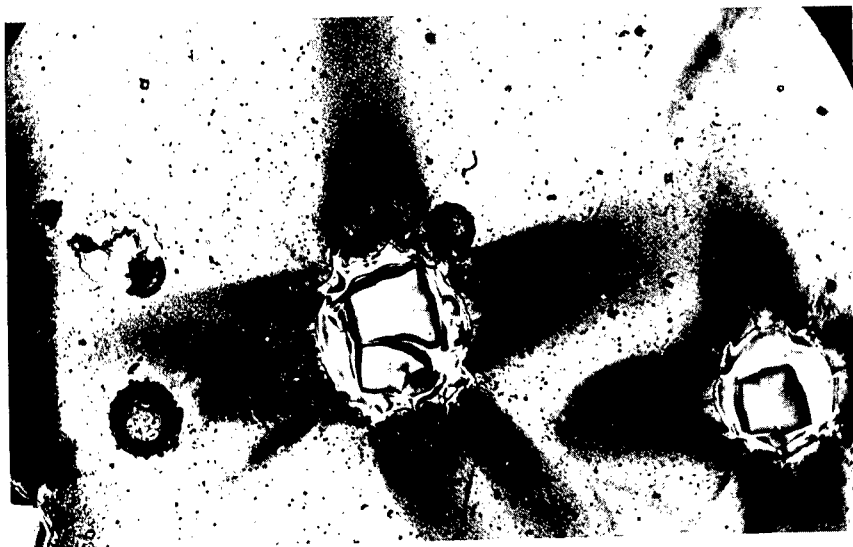
FIGURE 76.—Tungsten particles on stainless-steel substrate.   Torch-to-substrate
distance, 4 inches.   X130.

to-substrate distances was conducted to determine the apparent bonding and particle morphology. On glass substrates, zirconia exhibited a typical flow pattern (figure 75), resulting from high-speed liquid drops striking a surface. At a distance of 8 inches the particle velocity is 330 ft/sec, and the temperature is about 1,500° F; this results in the particle being flattened only slightly against the substrate with a few flow lines present. Tungsten particles undergo extreme flattening out to 5 inches (235 ft/sec and 2,300° F), and are still obviously deformed at a 9-inch distance. Zirconia splashed more than tungsten at a given distance. The particle velocities, temperature and cross section of zirconia particles sprayed on glass are given in table 27.

When stainless steel substrates were used, zirconia sprayed through a distance of 3 inches exhibited some insignificant adherence and most particles fell off. Tungsten adherence was excellent and some basal stringers were present as can be seen in figure 76. Again on tungsten substrates, zirconia exhibited no adherence at any working distance. Tungsten particles deformed on impact, but fell off leaving a splash pattern outlined by a ring, probably composed of tungsten oxide. Spraying with nitrogen improved the zirconia adherence slightly. Neither zirconia nor tungsten adhered to copper substrate though the copper surface pitted under the particle impact area.

From these experiments it was concluded that both zirconia and tungsten particles possessed sufficient temperature and kinetic energy to
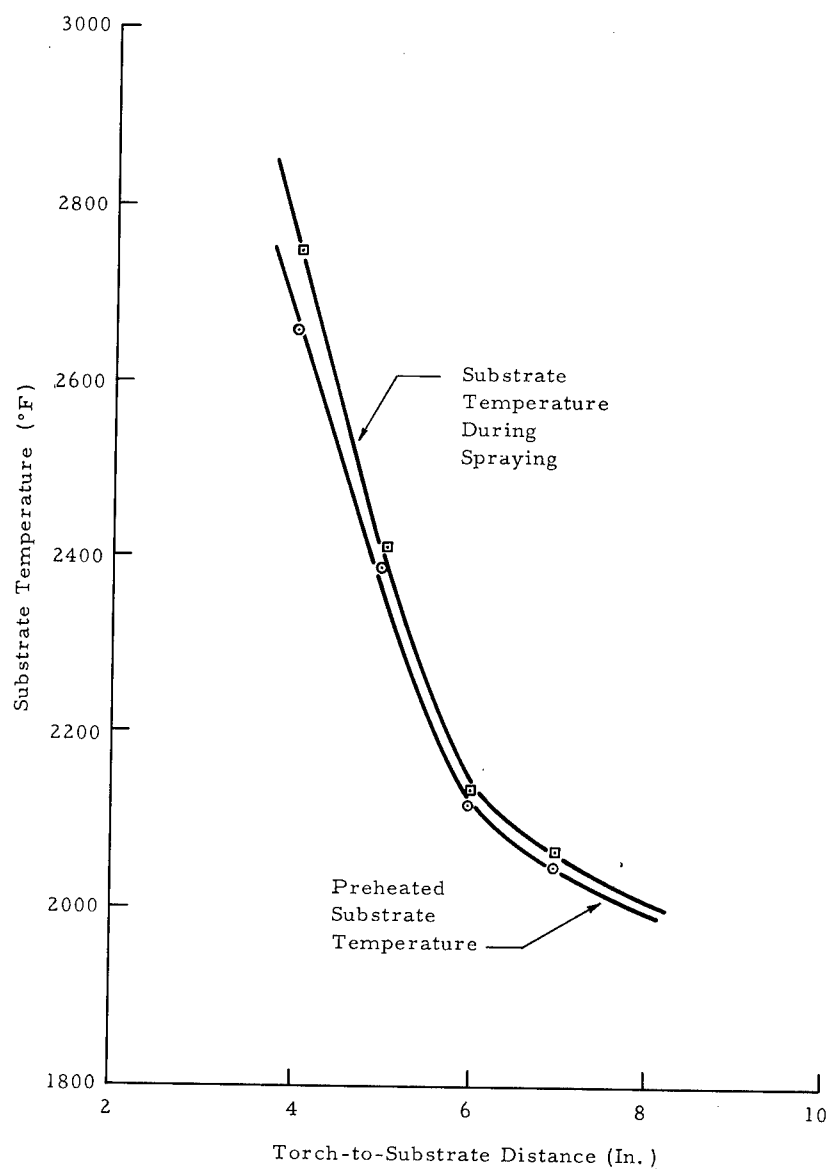
FIGURE 77.—Variation of substrate temperature with torch-to-substrate distance.

deform against substrate surfaces at reasonable working distances. Coating adherence to polished substrates was controlled by one major variable, the thermal conductivity of the substrate.

Subsequently Grisaffe and Spitzig (ref. 4) investigated the effect of substrate heating, since this is equivalent to decreasing substrate con-
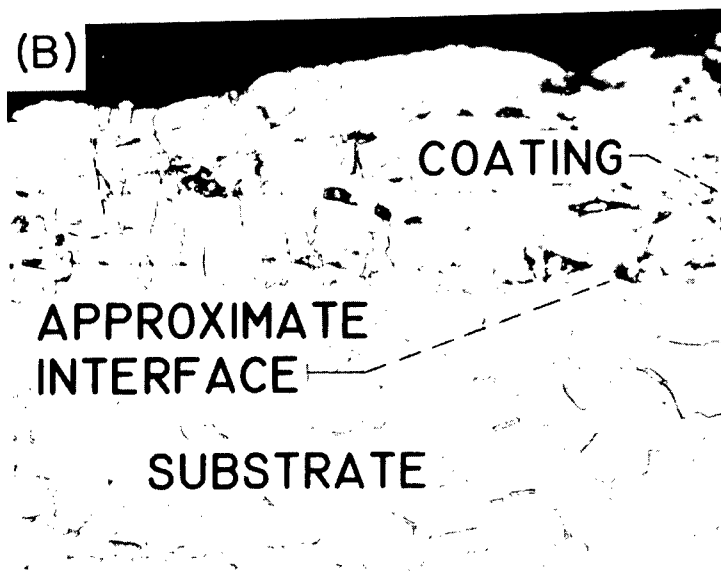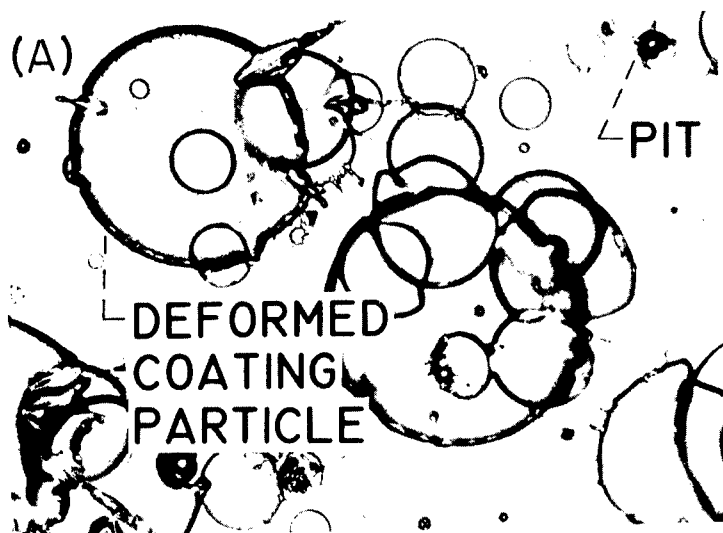
FIGURE 78.—As-Sprayed and cross section views for a 4-inch torch-to-substrate distance. Substrate temperature, −2700° F. (a) Particles on substrate. Etchant, Marakami's reagent; X250. (b) Particle cross section. Etchant, Murakami's reagent; X500.

ductivity by keeping the particle-substrate temperature elevated for a given time. Metallurgically-polished tungsten substrates were heated in a nitrogen atmosphere to various temperatures from 2,000° to 2,700° F using the arc-plasma as the heat source (fig. 77) and were sprayed with tungsten particles.

Examination of coatings sprayed at 4 inches and a substrate temperature of 2,700° F revealed that pits in the surface were not filled from adjacent particles though columnar grains perpendicular to the recrystallized structure of the substrate were present. Electron photomicrographs indicated the original interface had been almost completely eliminated by substrate grains growing into the coating through more than one layer of deformed particles, as indicated by the presence of isolated internal pores. Except for the grain configuration, no evidence was found to differentiate between the coating-substrate boundary and any other grain boundary.

With a working distance of 5 inches the substrate temperature was 2,400° F and changes in microstructure arose from an increased number of pits and incompletely deformed particles. The particle-to-particle interfaces were completely eliminated even though the substrate did not recrystallize. The original interface was marked with a line of pores. The coating assumed a columnar grain structure normal to the interface which is clearly shown in figure 78. This is particularly important since usually hot-sprayed metal coatings show a lamellar structure parallel to the interface. Columnar grain growth is typical of chemical vapor-deposited materials and materials which undergo grain growth when large temperature gradients are present. The attainment of what may be described as a metallurgical bond, by rapid short-range diffusion at the coating-substrate interface without altering the "as-worked" substructure, is a significant achievement in understanding and using the fundamentals of metal-to-metal coating adherence.

More recently Grisaffe and Spitzig (ref. 5) studied the interface formed between plasma-sprayed tungsten particles and room temperature polished AISI 304 stainless steel, with metallography electron microprobe, electron-microphotographs, and microhardness testing. Interdiffusion of the tungsten particles and stainless substrate form an alloy whose properties are similar to a stainless steel containing 5 to 6 weight/percent tungsten. It appears this alloy was formed by rapid solid-state interdiffusion. Figure 79 illustrates a typical cross section of an individual tungsten particle adhering to the 304 stainless steel surface. The electron microphotograph more clearly delineates the heat-affected zone adjacent to the tungsten particle. The line of etch pits separating the heat-affected zone from the rest of the 304 stainless steel is shown in figure 80.
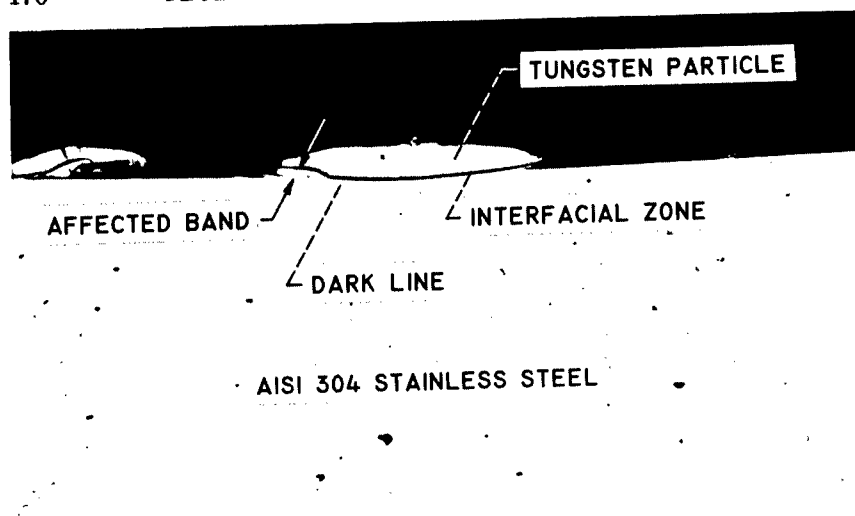
FIGURE 79.—Cross section of tungsten particle on AISI 304 stainless steel; etchant: oxalic acid, 10 percent solution; X290
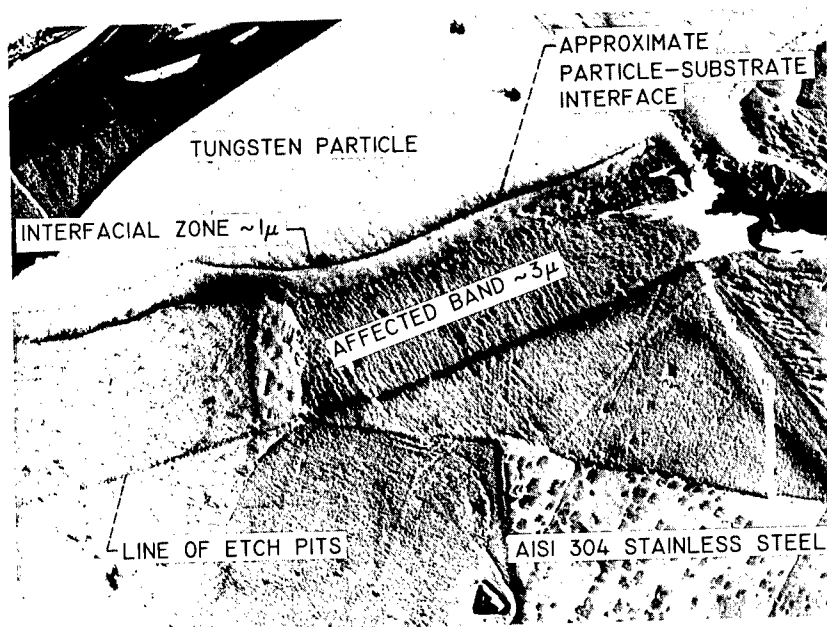
FIGURE 80.—Tungsten—AISI 304 stainless-steel interface; etchant: oxalic acid, 10 percent solution; X5,600.

Development of Pantograph Attitude-Controlled Flame Spray Equipment

The application of uniform thickness layers of thermal insulation coatings to the interior of the XLR–99 engine used on the X–15 Research Aircraft is quite difficult due to the restricted working space and lack of visibility. The repair and refurnishing of used coatings was even more difficult. However, the time consumed and the expense involved motivated Ottinger, Harwell, Ballard, and Fabian (ref. 6) to develop a pantograph-type, attitude-controlled, arc-plasma, spray apparatus which greatly facilitated repair work.

This equipment (fig. 81) consists of a rotating carriage and drive device which holds the XLR–99 engine and rotates it during the spraying operation. The flame-spray gun is mounted on the left end of a balance arm (out of sight just inside the engine). The location of the spray gun is determined by the tracing head at the right end of the balance arm as it follows the metal profile. Since the distance between the work and the gun is of critical importance, this device automatically assures the proper distance and the optimum coating. Figure 82 is a view of the spray gun extended up into the rocket nozzle.

The pantograph-controlled concept is not new; however, its application to rocket-nozzle repair has greatly facilitated the relining of coatings at less cost and a probable improvement of coating properties.

CHEMICAL VAPOR-DEPOSITION COATING TECHNIQUES

Vapor deposition is a useful coating process for producing a multitude of metallic, ceramic, and intermetallic coatings on a variety of substrates.
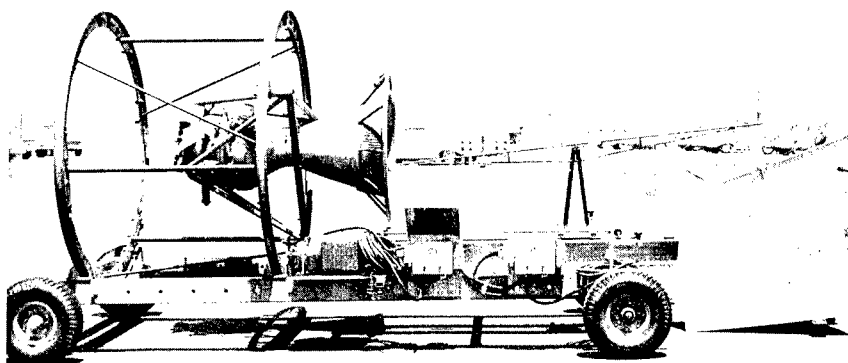
FIGURE 81.—General view of pantograph-directed arc-plasma-spraying equipment.
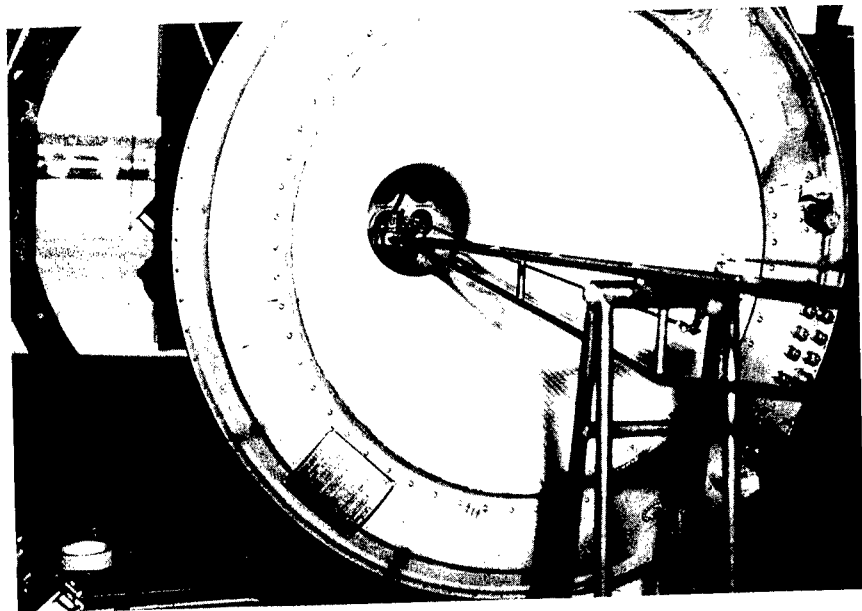
FIGURE 82.—Pantograph-controlled flame-spray inside rocket nozzle throat in spraying position.

The basic process depends upon the thermal decomposition, reduction, or displacement of different ions from gas molecules to a heated substrate. The technology of vapor deposition coatings, their general utility, and limitations were discussed fully in the definitive review by Powell, Campbell and Gonser (ref. 7). High-temperature vapor-deposition coatings have been more recently reviewed by Huminik (ref. 8). Information related to the fundamental chemical and physical processes of vapor deposition were detailed and elucidated, insofar as they are known, by Battelle Memorial Institute (ref. 9).

TUNGSTEN COATINGS BY THE BROMIDE PROCESS

Original work on the deposition of tungsten coatings on tungsten substrates by thermal decomposition of tungsten bromides was undertaken by Caves (ref. 10). While only tungsten coatings were prepared by the bromide decomposition process, the method is generally applicable to most of the transition metals. Van Arkel and de Boer (ref. 11) originated the iodide process which has been subsequently extended to the other halides, chlorine and fluorine. The bromides had not been previously used. However, due to general free-energy considerations, there was the promise of lower deposition temperatures. For many applications this lower deposition temperature is useful and desirable.

The basic coating process depends upon the following reactions:
1. Preparation.

$$W + 3Br_2 \quad \overset{\approx\ 900°\ F}{\longrightarrow} \quad \begin{array}{l} WBr_6 \\ WBr_5 \quad \text{Sublimes above} \\ WBr_4 \qquad 450°\ F \\ WBr_3 \end{array}$$
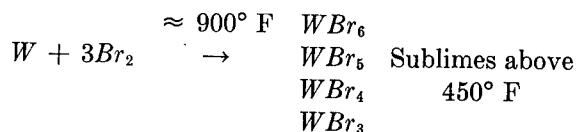
2. Coating Reaction.

$$WBr_6 \quad \overset{>\ 2,400°\ F}{\underset{<\ 2,000°\ F}{\overset{\longrightarrow}{\longleftarrow}}} \quad W + 6Br$$
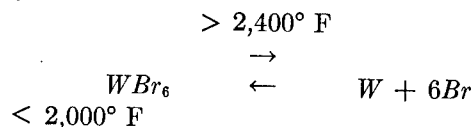
It is possible to establish a closed-system reaction chamber because the formation temperature of tungsten bromide vapor is well below the decomposition or deposition temperature. Tungsten metal must be provided at temperatures above 2,400° F, in order to provide a driving force in a sealed-chamber process.

The experimental apparatus used was a fused-silica-glass reaction chamber with the remainder of the system being borosilicate glass. WBr_6 was prepared by placing tungsten fragments in the bottom of the fused silica tube which was lowered into a 1,500° F furnace. The sample substrate was a 20-mil-diameter tungsten wire surrounded by a radiation shield and connected to each side of a split susceptor within the reaction chamber. A 15-Kva, 10,000-cycle induction unit supplied power to a novel combined induction-resistance system which eliminated the need for large power feed-throughs in the 900° F reaction chamber.

After the system was evacuated and outgassed at a pressure of 5×10^{-8} Torr, the pumping tube was collapsed and sealed off with hand torches, to isolate the system. A solenoid-actuated plunger broke open the bromine capsule to introduce bromine into the system. Residual-trace oxygen was removed by heating the entire reaction chamber walls, except for a cold finger cooled with liquid air. Any oxygen present reacted with tungsten bromide to form suboxides which condensed in the cold finger as yellow or orange deposits. When black tungsten bromide crystals appeared at about 450° F the cold finger was sealed off.

COATING OF TEST SPECIMENS

Power was supplied to the susceptor to bring the specimen to a temperature of 2,000° F or more which was held while the coating was applied. Studies were made of the effect of altering the WBr_6 vapor pressure by varying the chamber temperature while holding the specimen wire temperature constant at 2,650° F. The chamber temperature was varied from 225° F to 725° F in 100° F increments. After establishing an optimum chamber temperature, the chamber temperature was held constant and the effect of varying the specimen temperature was studied. The

specimen temperature was varied from 2,000° F to 2,800° F in 100° F increments.

RESULTS

The optimum halide preparation temperature was found to be near 625° F, and coatings were obtained on all specimens held at temperatures above 2,000° F. While coating growth rates were slow at lower temperatures (5 mils/44 hr) at the optimum temperature of 2,400 to 2,500° F, the coating rate was 1 mil/min. Exterior surfaces were rough by virtue of preferential grain growth on certain crystal surfaces. Roughness increased with increasing temperatures.

Microstructure examination indicated that the interface between the wire and the coating was free of pores or second phases. Bonding was considered excellent. The deposited tungsten exhibited the grain-growth structure of columnar grains typical of vapor-deposition coatings. Some specimens were occasionally observed with concentric rings of holes in the deposited coatings. This effect was thought to be due to vaporization of impurities from the reaction chamber glass walls, although chemical analysis did not confirm this observation.

Microhardness measurements gave a value of 334 for coated materials and 390 for the wires used as substrate as compared with 340 which is commonly observed in commercial electron-beam-refined tungsten.

The chemical and spectrographic analysis is given in table 28. The presence of molybdenum is accounted for by the presence of 570 ppm molybdenum in the susceptor, which apparently was transported to the sample. This could be easily overcome by using high-purity tungsten components in the apparatus. The presence of carbon and sulfur in the coatings indicated that vacuum grease or pump oil contaminated the system prior to pinch off. Because gases embrittle tungsten severely, it is important to note that hydrogen, oxygen, and nitrogen concentrations are low. In fact, they are below the accepted limit of accurate analysis, but are nonetheless significant by comparison with the specimen wire material.

Thin coatings, 7 mils thick, of tungsten were deposited on tungsten threaded-screws. Conformity of the coatings to the substrate surface was good and the coatings were essentially composed of a single grain layer.

SPUTTERING OF THIN FILMS ON ROLLED SHEET SUBSTRATE

Cathodic sputtering was discovered by W. R. Grove in 1852, but until recently its use in technology has been insignificant. Sputtering is accomplished by the excitation of noble-gas ions, usually argon, and imparting to them high kinetic energies by acceleration in a high potential electric field. The material to be sputtered is located at the cathode and

TABLE 28.—*Chemical and Spectrographic Analysis of Tungsten*

Trace Elements		Concentration: Parts Per Million (ppm)		
Element	Analyses Minimums,[a] ppm	Materials of Con- struction	Coating and 20-Mil Wire Core[b]	Control 20- Mil Core Wire
Found in Coating:				
Carbon_____	2	42 to 86	38	40
Molybdenum_____	10	[c]10 to 570	30	10
Sulfur_____	10	18	20	18
Hydrogn_____	1	0.86 to 1	[d]0.0007	0.5
Oxygen_____	4	1 to 140	[d]0.5	6.4
Nitrogen_____	(Vac. Fus.[c])	2.9 to 27	[d]0.02	2.0
Not Found in Coating:				
Aluminum_____	2	10 to 15	<2	<2
Boron_____	2	<2_____	<2	<2
Calcium_____	10	<10_____	<10	<10
Chromium_____	10	10 to 30_	<10	<10
Copper_____	1	1 to 10_	<1	<1
Iron_____	2	15 to 90_	<2	20
Nickel_____	2	15 to 60_	<2	8
Silicon_____	3	10 to 90_	<3	<3
Sodium_____	10	<10_____	<10	<10

[a] The lowest limit of accurate determination.

[b] Estimated concentrations (in ppm) for selected trace elements, obtained as preliminary results with a more sensitive spectrographic procedure at the Lewis laboratory, are as follows: Al, 1; B, 0.3; Ca, 0.4; Co, 0.5; Cr, 1; Cu, 0.3; Fe, 0.7; Mg, 0.1; Ni, 0.3; and Ti, 0.4.

[c] See text, section headed "Chemical and Spectrographic Analysis."

[d] Indicative of relative amount; see text, section headed "Chemical and Spectro- graphic Analyses."

the collision of the gas ions with the material removes ions from the cathode which are deposited on the anode. Films produced by cathode sputtering are adherent and can be produced in controlled thicknesses from any known substance.

Evans (ref. 12), NASA Lewis Research Center, has developed new, highly-automated equipment to produce coatings useful for photovoltaic cell experiments. Figure 83 is a schematic diagram of this system. The significant developments in this apparatus are the numerous steps taken to assure a clean vacuum, and the controls used in obtaining uniform, controlled coatings. The control system pictured in figure 84 is located between two sputtering chambers. The power supply provides a potential range from 400 to 5,000 v and a current density ranging from microamperes to several milliamperes per square centimeter of cathode surface. Water cooling of the cathode allows for precise temperature control by removing heat generated by ion impact. Film thickness is determined by the voltage and current selected which are automatically controlled.
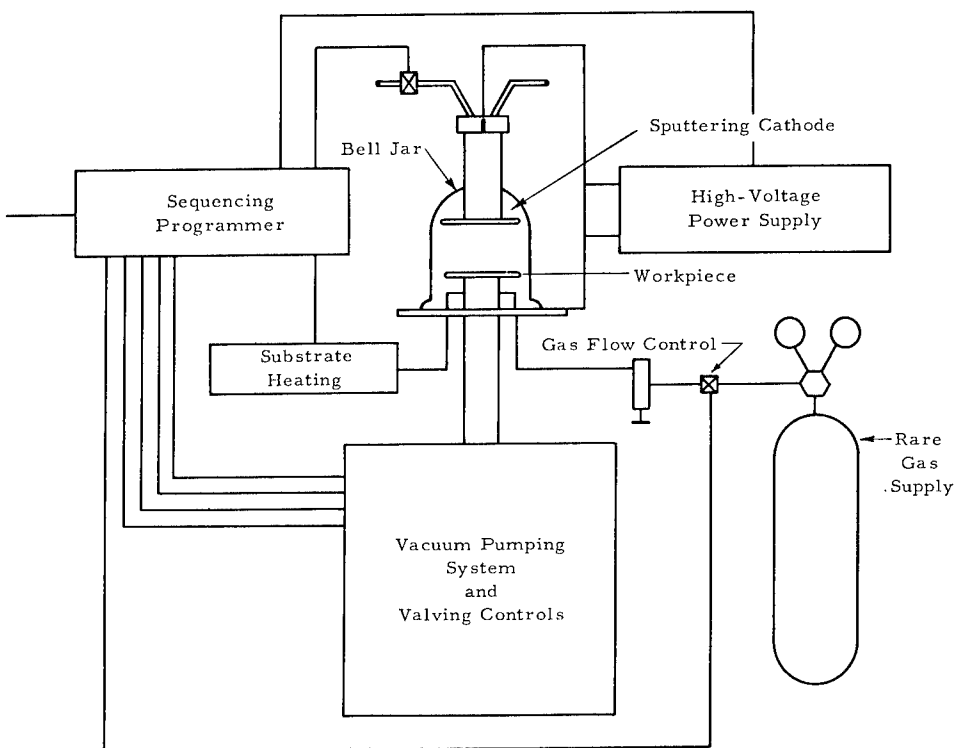
FIGURE 83.—Block diagram of automated film sputtering system.

The vacuum system developed is of special interest as a method used to obtain a controlled uncontaminated pressure within the sputtering chamber.   In the sputtering of photovoltaic cell materials, even minute amounts of impurity gases or oils will alter the film properties. Therefore, it is necessary to purge the system by reducing it to vacuum several times before the noble sputtering gas is introduced.   All seals are constructed of Viton A material and cooled where required to maintain ambient temperatures.

The vacuum pumping system consists of a mechanical pump and a diffusion pump filled with silicone pumping fluids. To prevent back-streaming from the pumping system to the chamber, three different traps are used.   Directly above the diffusion pump is located an antimigration, absorption-zeolite trap, followed by a liquid nitrogen chevron baffle, and for the larger system a thermoelectric baffle.

Program-cycling timers are driven by clock drives which may be adjusted to allow a complete run to range from minutes to days.   The
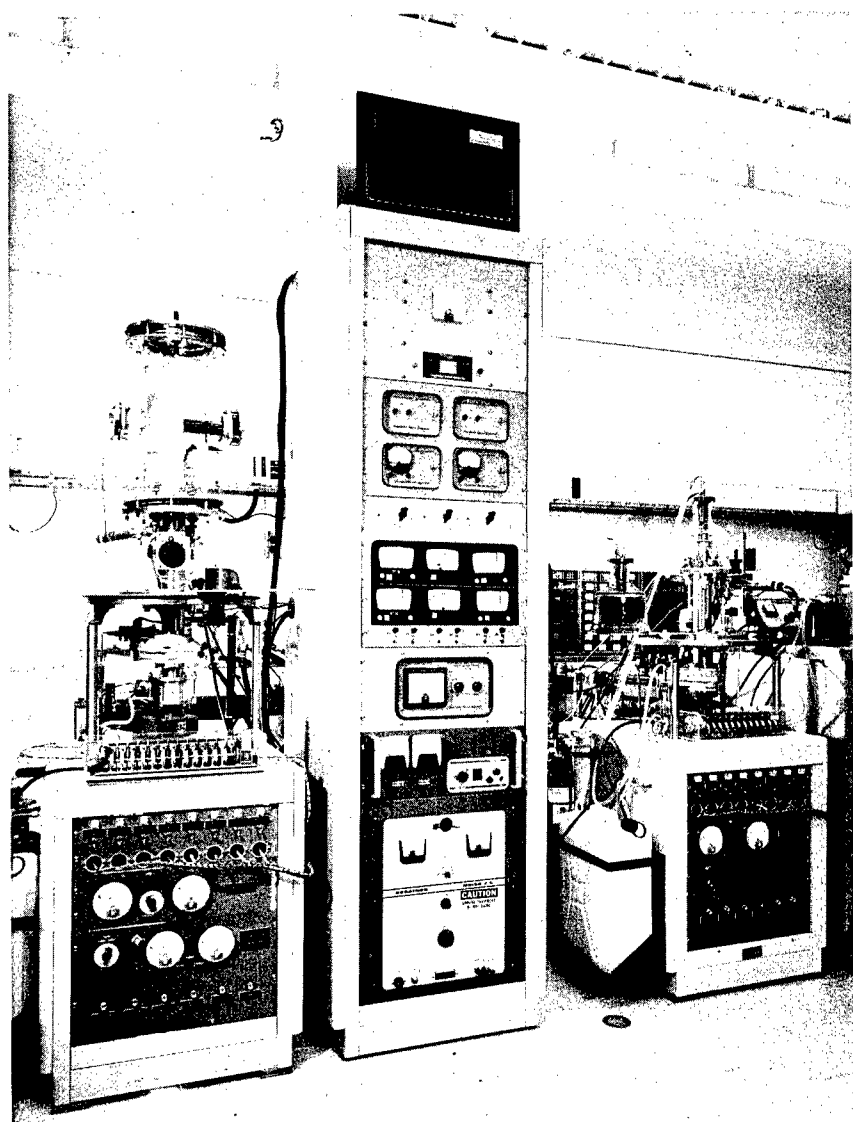
FIGURE 84.—Automated cathode sputtering apparatus for depositing inorganic coatings.

pumpdown, purging cycles, and liquid nitrogen feed, are all programmed. All valves are solenoid or solenoid-pneumatic and are designed to protect the apparatus. The flow rate of the inert gas into the chamber is controlled, as is the pumping rate, to fix the chamber pressure within narrow limits, usually in a 100μ gas pressure range.

A roller mechanism has been proposed which pulls a film of substrate material over the interior surface of a split cylindrical anode. The cathode is mounted coaxially in the center of the anode. Thus, long rolls of film of large area can be uniformly sputtered with different layers. A completed photovoltaic cell is composed of six layers over the substrate. These layers are: (1) a deposited silver electrode strip; (2) a transparent and conductive layer of indium and tin oxide; (3) a deposited cadmium sulfide layer; (4) sputtered reactive copper oxide; (5) a deposited outer silver electrode strip; and, (6) a polymerized-coating of silicone moisture-barrier over the completed cell. At the present time, photovoltaic cells convert about 3 percent of the solar energy into electricity; the goal is to reach the present 15 percent efficiency of silicon cells.

SUBSTRATE PREPARATION BY TUMBLING

D. R. Rummler (ref. 13), Structures Research Division, NASA Langley Research Center, investigated the effect of various substrate preparation procedures, particularly as pertaining to edge effects on the oxidation-resistant coatings applied to Mo–0.5 Ti alloy sheet. Small test coupons $\frac{3}{4}$ inch by $1\frac{1}{2}$ inches were fabricated from stress-relieved 12-mil-thick sheet stock. The following edge treatments were tested.

1. Warm sheared to size

2. Machined to size and the edges hand broken with emery

3. Machined to size with 0.125-inch radii at corners. All edges were then dry tumbled in an abrasive mix of No. 180 silicon carbides grit and $\frac{1}{4}$-inch to $\frac{5}{8}$-inch rounded pebbles.

All specimens were fabricated by NASA and sent to several coating suppliers for the application of their optimum coating for the following performance guideline specifications:

1. Oxidation resistance of at least 10 hours at 2,500° F in static air.

2. A maximum allowable decrease in room temperature elongation of 25 percent.

3. A maximum allowable weight gain of 25 percent.

Suppliers were requested to apply the same coating to all specimens (other tests were conducted at the same time) and to use normal cleaning and surface preparation procedures prior to coating. The various

coating suppliers, their coating designations, substrate thickness before and after coating, coating thickness and the weight gain of the coated specimens are given in table 29.

Testing consisted of constant static-air exposure of a sample placed inside a zircon boat suspended inside a 2,500° F vertical tube furnace. A 10 percent weight loss was used as the failure criterion. If failure was not observed after 250 hr, the test was normally terminated. Metallographic examination of the "as-coated" samples indicated that coating continuity was superior on the machined-and-tumbled specimens and somewhat less continuous on the sheared samples and the machined-and-broken specimens. Representative microstructures of the three various "as-coated" specimens are presented in figure 85.

The results of these tests indicate that edge preparation is an important parameter of coating life. The specimens prepared by machining and tumbling were superior in a majority of cases to the specimens prepared by the other two methods from a working standpoint. The AMF-glassed tumbled specimen was stable for 450 hr, while the broken-edge sample failed after 120 hr. In only two cases, the AMF-not-glassed and the Chance Vought CV specimens, did the tumbled specimens exhibit shorter test-exposure life. In both of these cases the difference was small and probably not significant.

Metallurgical examination indicated that the partially recrystallized substrate of the tumbled and sheared edge suggest that these two edge preparations are less severe than the fully recrystallized substrate observed on the machined edge. The lower recrystallization temperature of the broken edge, which may be the result of the more severe fabrication process and the accompanying higher residual stresses, probably contribute to a shorter coating life.

COMMERCIAL IMPLICATIONS

Although the NASA contributions cited in this report may or may not lead directly to useful commercial processes or products, they are of significant value to the coating technology. Beyond this general statement, an attempt will be made to point out specific application potentialities which may or may not be currently economical, but are technically feasible.

COATING WITH HIGH-TEMPERATURE PARTICLES

The hot-spraying of metals or metallizing has long been a useful and important commercial process. The development of equipment by commercial manufacturers to meet aerospace needs will result in apparatus that has higher capacity both with respect to rate of deposition and
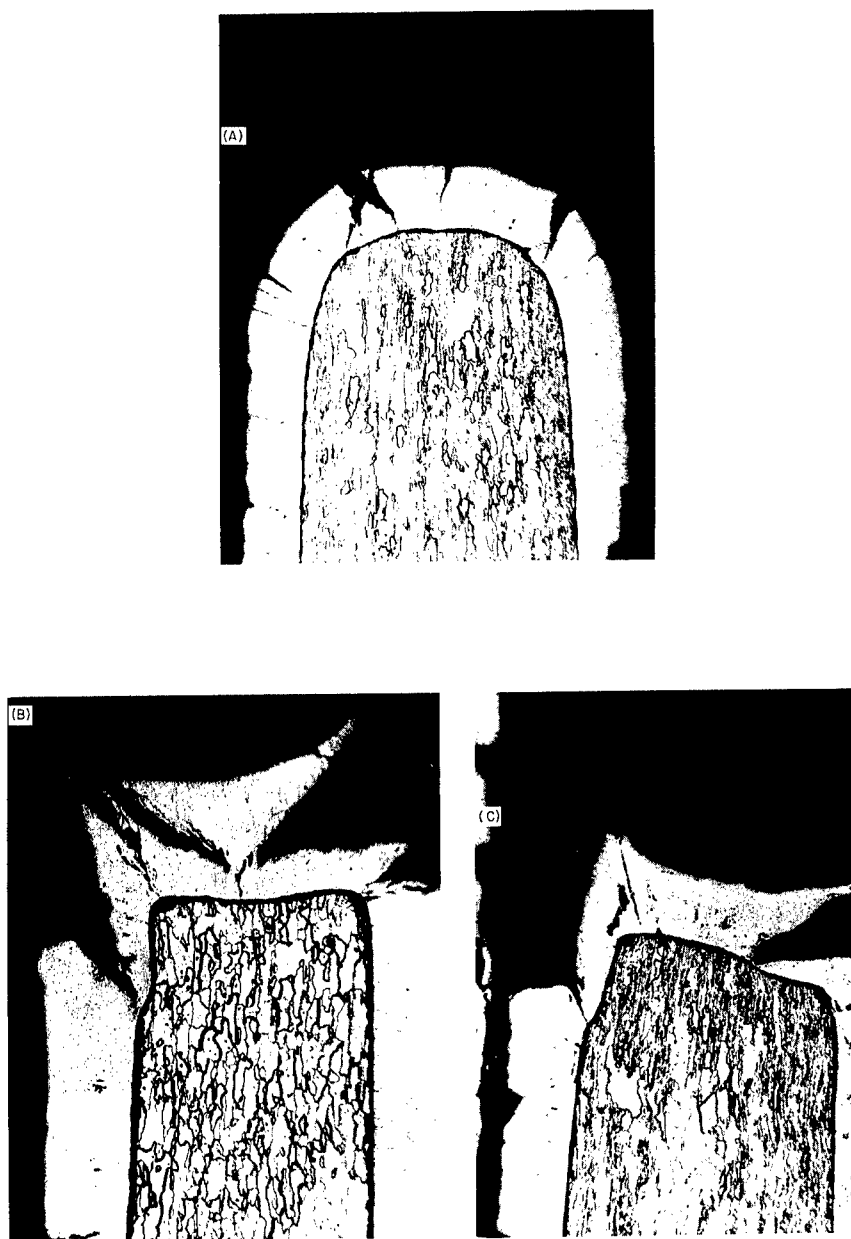
FIGURE 85.—Coating continuity of coatings with different edge preparation procedures. (A) sheared, (B) machined-and-hand-broken corners, (C) machined-and-tumbled.

TABLE 29.—*Coatings Under Study*

Supplier	Designation	Average Coating[a] Thickness (in.)	Substrate Thickness (in.)[a]		Weight Change (percent)
			Before Coating	After Coating	
American Machine & Foundry	AMF (Glassed)[b]	0.0017	0.0122	0.0092	2.20
Do	AMF (Not Glassed)	0.0017	0.0122	0.0099	2.20
Boreing	Disil	0.0015	0.0108	0.0081	-3.81
Chance Vought	C-V	0.0014	0.0120	0.0106	3.43
Chromalloy	W-2	0.0012	0.0121	0.0109	4.40
Pfaudler	PFR-5	0.0023	0.0118	0.0091	13.67
Pfaudler	PFR-6	0.0019	0.0116	0.0097	7.92

NOTES: [a] Based on cross section of tumbled specimen.   [b] Preglassed 1 hr at 2800° F by AMF.

temperatures. The work of Grisaffe and Spitzig in understanding the fundamentals of the kinetic and thermal interactions between the heat source and the particles being sprayed is of particular significance. The nature of the bonding between the sprayed coating and the substrate will yield avenues for process development; which, until the present, have been at best trial-and-error studies.

The development of metallurgically-bonded tungsten coatings to tungsten substrate opens the way for a new method of tungsten fabrication and repair, at the very least. More likely the application of this information will allow metal shapes to be altered after service. Thus, rather than scrapping a complex piece because of local wear, the metal can be rebuilt and refinished. Frequently, pieces of metal must be cut away to produce a final shape. In the future, more use will be made of added metal to simple starting geometries. It is too much to expect the immediate adoption of this method for either repair or new work. Designers must be given specific process information before they dare specify the use of this method for a particular application. In addition there will be some pure human inertia. For repair and rebuilding applications we must be less optimistic about the utilization of a process which is truly economical. It is probable that social and economic forces as well as industrial organizations focus on selling new items to our consumers rather than providing efficient repair services.

However, Gibeaut and Maykuth (ref. 14) report the work of Grisaffe in using his process of arc-plasma spraying to solve two particular NASA requirements relating to refractory metal restoration. In the first example a tungsten furnace-element evaporated and was unsatisfactory. This element was restored to service by replacing the lost metal by spraying. In the second example, rolls constructed of molybdenum used as a part of a high-temperature metal rolling program became scored in use. Grinding restored the surface finish, but at the expense of material removal. Eventually the rolls had to be restored by metal additions. Such rolls were rebuilt by the arc-plasma-spraying of molybdenum upon the surfaces and then grinding to the desired surface finish.

The perfection of hot-metal spray equipment may make it possible to apply anticorrosion coatings of metals and ceramics to steel and other ferrous materials. The advantage of these coatings would be that useful protective lives of ten, twenty, or thirty years should be possible. Thus, the constant need for expensive repainting could be eliminated or reduced.

Table 30, prepared by Metco, Inc., lists a number of materials available as experimental powders and possible areas of usefulness for these materials. We want to make it clear that NASA has not developed these materials; however, NASA has contributed significantly to the technology as a whole, both as a pioneering consumer and through research and development.

PANTOGRAPH-CONTROLLED FLAME SPRAY

Several commercial companies mount their apparatus on different machines for controlled spraying. Equipment similar to the NASA apparatus will be adapted and modified for commercial applications as the needs arise. One would expect that tape-controlled spraying equipment will make its appearance as an automated production tool for special production purposes.

BROMIDE-TUNGSTEN VAPOR COATING PROCESS

NASA personnel have demonstrated the technical feasibility of coating tungsten onto tungsten substrates using the bromide process. Operational parameters were optimized and coatings were produced with a chemical purity superior to commercial tungsten. Specific commercial applications of this method for tungsten and development of other metal-bromide processes must await industrial exploitation. The cost evaluation and industrial process development will depend upon further research.

AUTOMATED CATHODIC-SPUTTERING EQUIPMENT

The NASA-developed automated-sputtering equipment should prove useful, not only for its current task of producing photovoltaic solar cells, but for the deposition of metals upon plastic films for decorative purposes and for the production of cryogenic insulations. As will be discussed later, the development of coating-technology for plastic films should make the use of solar heating economically as well as technically feasible. (See Thermophototropic Coatings.)

SUBSTRATE PREPARATION BY TUMBLING

Tumbling is an accepted industrial process for many applications. Its importance as a commercial process for refractory metal substrate preparation will depend upon the utilization of refractory metals in general.

TABLE 30.—*Experimental Powders*

*Data Supplied by Metco Inc.**

Material Number	Material	Use Code	Melting Point °F	Expansion Coefficient ×10⁻⁶/°F	Texture as Sprayed	Porosity	Bonding Properties	Possible Areas of Usefulness
XP 1101	Chromium	A&B	3435	3.67 212° F–1290° F	Medium	Medium	Excellent	Bearing surfaces at low to medium temperatures. Corrosion resistant coatings when properly sealed.
XP 1102	Cobalt	A&C	2715	6.84 68° F–212° F	Fine	Low	Excellent	Dense, strongly adherent coatings. Mixture with ceramics for cermets.
XP 1104	Nickel (Coarse)	A&B	2650	7.39–9.04 212° F–1652° F	Medium	Medium	Good	Corrosion resistant coatings when properly sealed, oxygen barrier coatings under ceramics.
XP 1105	Nickel (Fine)	C	2650	7.39–9.04 212° F–1652° F	Fine	Low	Good	Corrosion resistant coatings when properly sealed, mixture with ceramics to form cermet coatings.
XP 1107	Chromium Carbide (Coarse)	A	3434	4.9, 68–248° F 6.1, 300–1800° F	Fine	Medium	Good	Wear resistant coatings.
XP 1108	Chromium Carbide (Fine)	C	3434	4.9, 68–248° F 6.1, 300–1800° F	Fine	Low	Good	Wear resistant coatings, mixture with metal powders for cermet coatings and wear resistance at higher temperatures.
PX 1109	60% Chromium Carbide-Cobalt Blend.	A&C	3434 2715	----------	Fine	Low	Excellent	Wear resistant coatings particularly on aluminum (and other non-ferrous materials excellent
XP 1110	Tungsten Carbide—12% Cobalt Aggregate.	A	Softening Pt. above 2715	----------	Fine Fine	Low	Very Good	Wear resistant coatings.
XP 1113	Rare Earth Oxides	A&B	Above 4000	----------	Fine	Medium	Very Good	Thermal barriers, combustion catalyst.

								Remarks
XP 1114	Titanium Oxide	A&B	3490	3.9-4.5 70° F-1100° F	Fine	Very Low	Excellent	Hard, abrasion resistant, minimum porosity coatings with excellent adhesion to base. For mixture with other ceramic and metal powders to improve physical properties of the coatings.
XP 1115	Zirconium Oxide, Hafnia Free, Lime Stabilized.	A&B	Approx. 4700	5.6, to 2200° F	Fine	Low	Good	Thermal barrier coatings for nuclear applications.
XP 1116	Zirconium Silicate	A&B	Approx. 3225 4390	3.05 70° F-2190° F	Medium	Medium	Good	Thermal barrier coatings.
XP 1117	Magnesium Zirconate	A&B	3830		Fine	Low	Good	Thermal barrier coatings. Resistant to wetting by various metals, and can be used for coating melting pots and allied equipment. Especially useful in lining graphite crucibles used in melting and refining uranium.
XP 1118	Calcium Zirconate	A&B	Approx. 4250	5.75, to 2200° F	Fine	Low	Very Good	Thermal barrier coatings. Resistant to wetting by various metals, and can be used for coating melting pots and allied equipment. Dense, hard, abrasion resistant coatings with very good bond.
XP 1119	40% Cobalt-Zirconia Blend	A&B	2715 4700		Fine	Low	Excellent	High temperature cermet coating. High hardness and abrasion resistance. Retards oxidation of base materials and excellent thermal shock resistance.
XP 1120	40% Nickel-Alumina Blend	A&B	2650 3700		Fine	Low	Very Good	High temperature coatings where thermal shock is a problem.
XP 1121	50% Titania-Alumina Blend	A&B	3490 3700		Fine	Very Low	Excellent	Useful where hard, abrasion resistant, smooth, strongly adherent coatings with less thermal shock resistance are required.
XP 1122	Tungsten Carbide	A	5200	6.2, to 77° F- 1570° F.	Fine	Low	Fair	Excellent blast erosion qualities as sprayed for high temperature applications, i.e., rocket nozzle coatings.

See footnote at end of table.

TABLE 30 (Continued).—Experimental Powders

Data Supplied by Metco Inc.*

Material Number	Material	Use Code	Melting Point °F	Expansion Coefficient ×10⁻⁶/°F	Texture as Sprayed	Porosity	Bonding Properties	Possible Areas of Usefulness
XP 1123	Fine Tungsten Carbide in Self-Fluxing Matrix Premium Grade	A	1900 (Matrix)	----------	Medium	Very Low	Excellent	Dense, high quality, wear resistant carbide coating without the need of fusing.
XP 1124	An 18 and 8 Type Stainless Steel.	C	2500 2550	8.9 32° F-212° F	Fine	Very Low	Excellent	Very dense, bright smooth machinable coatings where hardness is not needed. For repair of bronze, stainless or alloy parts. Example: Cavitation in stainless steel vessels.
XP 1125	Nickel (80%) Chromium (20%).	C	2550	9.8 158° F-1832° F	Fine	Very Low	Excellent	Resistant to heat, corrosion and oxidation. For general use where very fine machine finish is needed.
XP 1126	Barium Titanate	A&B	3010	----------	Fine	Very Low	Good	Dielectric Material.
XP 1127	Chromium Oxide	A	3614	5.0, to 70° F- 2000° F	----	Very Low	Good	Excellent wear resistant and high temperature resistant coating.
XP 1128†	30% "Nickel Aluminide"- Alumina Blend.	A&B	----	----------	Fine	Low	Very Good	Useful where hard, smooth, dense cermet coatings of low porosity are required. Recommended for construction of gradated coatings for thermal barriers, especially where thermal shock is a problem.
XP 1129†	70% "Nickel Aluminide"- Alumina Blend.	A&B	----	----------	Medium	Low	Excellent	Useful where hard, smooth, dense cermet coatings of low porosity are required. Recommended for construction of gradated coatings for thermal barriers, especially where thermal shock is a problem.

	Material							Remarks
XP 1130†	35% "Nickel Aluminide"-Zirconia Blend.	A&B	------	------	Fine	Low	Very Good	Useful where hard, smooth, dense cermet coatings of low porosity are required. Recommended for construction of gradated coatings for thermal barriers, expecially where thermal shock is a problem.
XP 1131†	65% "Nickel Aluminide"-Zirconia Blend.	A&B	------	------	Medium	Low	Excellent	Useful where hard, smooth, dense cermet coatings of low porosity are required. Recommended for construction of gradated coatings for thermal barrier, expecially where thermal shock is a problem.
XP 1132	Columbium	A	4532	------	Fine	Medium	Excellent Self-Bonding to Steel.	Light weight refractory metal. Coating is very hard and abrasion resistant.
XP 1133	Molybdenum Disilicide	A	3700 (approx.)	------	Fine	------	Fair to Good.	Oxidation protection at higher temperatures, such as for graphite.
XP 1134	Magnesia Alumina Spinel	A&B	3530	------	Fine	Low	Very Good	High abrasion and wear resistance. Resistant to attack by molten glass, and some molten salts and slags except iron oxide. Not attacked by pure silica until over melting point. Electrical insulator.
XP 1135	Boron Crystalline	A	4000	4.6 40–1382° F	Fine	Low	Excellent	Dense, heat resistant coatings form self-heating oxide films in oxidizing atmosphere. Possible application as neutron absorber in reactors.
XP 1136	Hexaboron Silicide	A	3540	3.5 78–1800° F	Fine	Low	Excellent	Self-healing protective coatings for substrates such as graphite. Application as neutron absorber.
XP 1137	Chromium Silicide Cr_3Si_2	A&B	2912–3092	------	Fine	Low	Excellent	Hard, dense coatings with excellent oxidation resistance at high temperatures. Good wear resistance at elevated temperatures. Thermo-Spray coatings are not as hard as Plasma Flame coatings.

See footnote at end of table.

TABLE 30 (Continued).—Experimental Powders

Data Supplied by Metco Inc.*

Material Number	Material	Use Code	Melting Point °F	Expansion Coefficient ×10⁻⁶/°F	Texture as Sprayed	Porosity	Bonding Properties	Possible Areas of Usefulness
XP 1138	Tin	A	449	14.9, 64-212° F	Medium	Very Low	Excellent	Electrical contacts.
XP 1139†	Tungsten Carbide-Self-fusing Blend	A	Softening Pt. Above 1900° F.		Fine	Very Low	Excellent Self-Bonding to Steel	For thin, wear-resistant coatings. Can be given a very high surface finish.
XP 1140	Yttrium Zirconate	A	Approx. 3812		Fine	Very Low	Good	Useful where hard, dense, glassy ceramic is required.
XP 1141	Silicon	A	2570	4.5, to 104° F			Fair	Protect graphite against oxidation.
XP 1142	Silver	C	1761	10.4, to 68° F	Fine	Very Low	Excellent	Electrical contacts.
XP 1143	Platinum	C	3217		Fine	Very Low	Very Good	Expecially corrosion resistant. Used for electrical contacts and high temperature electrical conductors. Not wet or attacked by molten glass.
XP 1144	Iron	A	2798				Good	Useful where magnetic coatings are required.
XP 1145	Nickel Oxide NiO	B	3794		Fine	Very Low	Very Good	High emissivity. Hard, dense refactory coatings for high temperature oxidizing atmospheres. May not be useful in high temperature reducing conditions.
XP 1146	Mullite (Aluminum Silicate)	A&B	3326		Fine	Low	Good	Very high hot strength and good thermal shock resistance. Resistant to wetting by many molten metals. Excellent dielectric.

XP 1147	Calcium Titanate	A&B	3580	----------	Fine	Very Low	Excellent	Useful where excellent dielectric coatings are required.
XP 1148	Kovar Sealing Glass	B	Soft 1300 Work 2040.	2.5	Fine	None After Fusing.	Fusion	Sealing metal-glass or metal-ceramic joints, if thermal expansions are closely matched. Excellent dielectric, when fused.

* Metco Inc., 1101 Prospect Ave., Westbury, L. I., New York.
† Patent Pending.

Measurement of Optical Properties of Coatings

Due to the need for more accurate optical data for temperature control purposes, NASA has purchased a sizeable number of commercial measurement apparatus to establish data on solar absorptance (α) and hemispherical emittance (ϵ). For some NASA requirements commercial apparatus was not available so NASA personnel developed or perfected apparatus that served functions different from available equipment. In some cases the end measurement may be identical, but for particularly vital data it is good scientific and technical practice to check measurements by separate independent methods.

Information concerning thermal radiation properties of solids is rather limited and all too frequently diffused through the literature. An important contribution to the technology of this field is the annual "Symposium on Thermal Radiation of Solids," jointly sponsored by NASA, the Aeronautical Systems Division, USAF, and the National Bureau of Standards. The first meeting was held at the University of Dayton, September, 1962, and resulted in a monumental volume, "Measurement of Thermal Radiation Properties of Solids," edited by Joseph C. Richmond (ref. 1) and published by NASA in 1963 as document NASA SP–31. (For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C., 20402. Price $3.50.)

The second symposium was held in San Francisco, California on March 4, 5, 6, 1964. The results of this meeting will be published in approximately two months. Information concerning future meetings can be obtained from Mr. James J. Gangler, NASA Headquarters, Washington, D.C. A marked increase in the rate of growth in the technology of radiation properties has resulted as a consequence of this Symposium.

The general importance of and requirements for optical measurements for thermal control surfaces for space vehicles was described in detail by Heller (ref. 2) of the NASA Marshall Space Flight Center. A comprehensive review of the principles of various possible optical measurements was given by Fussell, Triolo, and Henniger (ref. 3) of the NASA Goddard Space Flight Center.

MEASUREMENT OF (α/ϵ) RATIO

Fussell, Triolo, and Henninger (ref. 4) have developed a device for measuring the solar absorptance and thermal emittance of spacecraft coatings by dynamic technique. The apparatus is similar in principle to that of Gordon (ref. 5).

The apparatus (figure 86) consists of five major components: (1) the vacuum system; (2) the solar simulator; (3) the liquid-nitrogen-cooled shroud; (4) the temperature recorder; and, (5) the solar intensity measur-
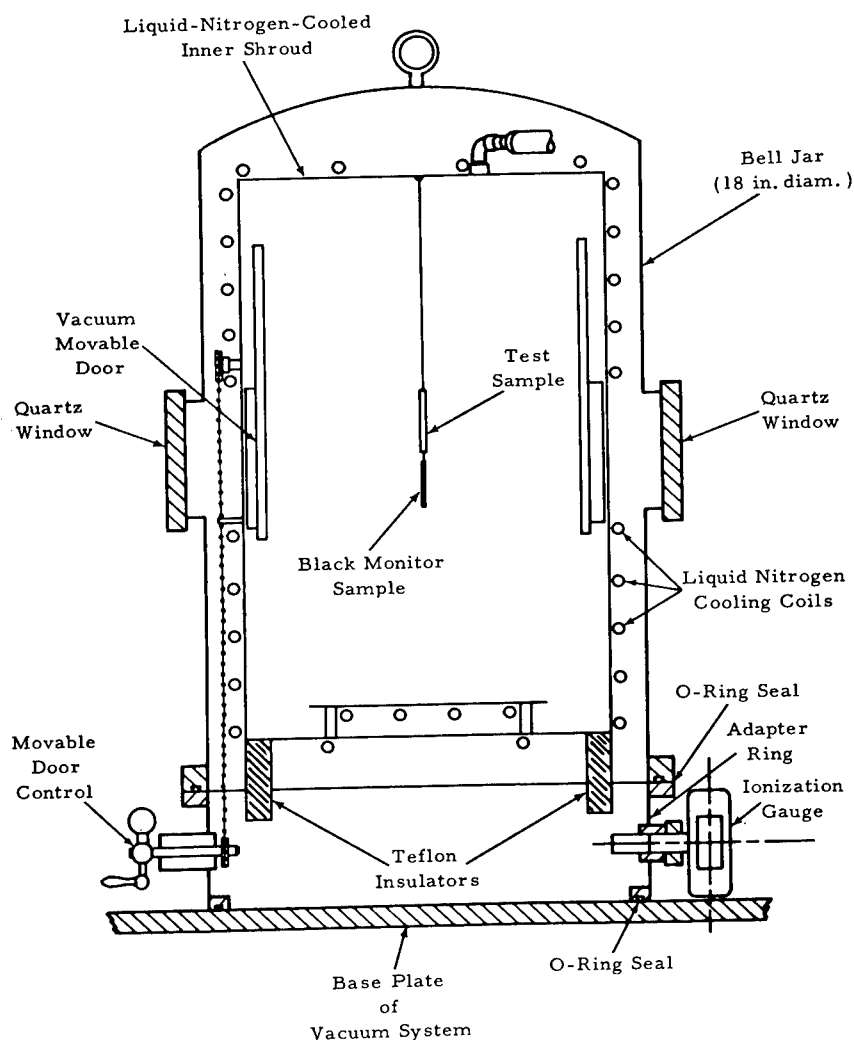
FIGURE 86.—Cross section view of the cooled shroud and vacuum system bell jar.
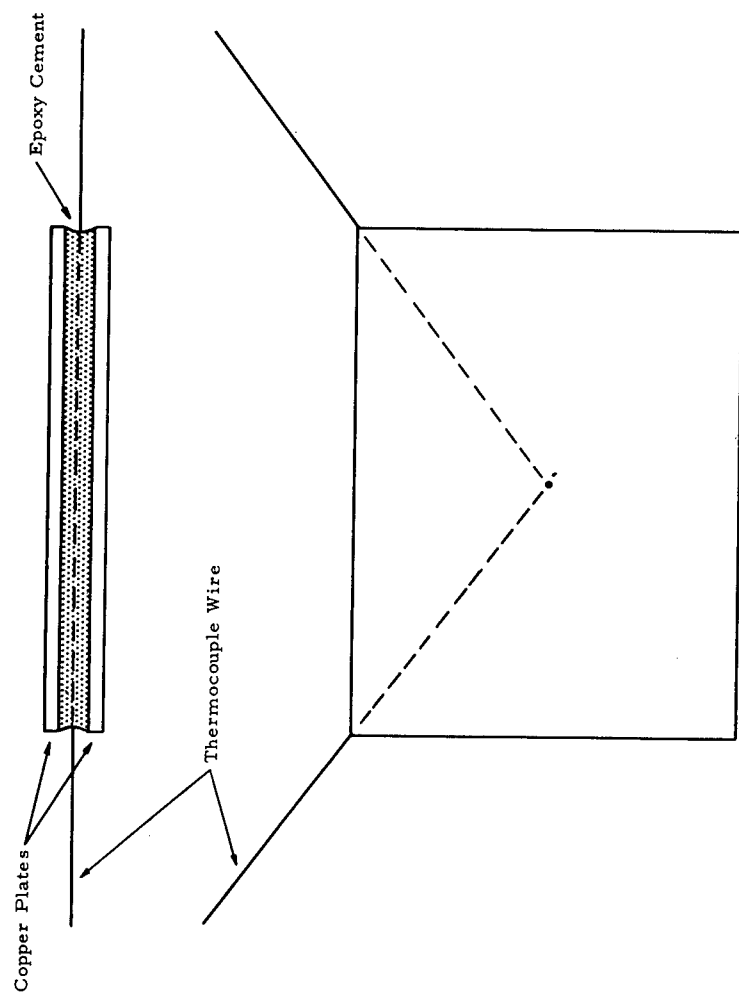
FIGURE 87.—Test sample thermocouple configuration.
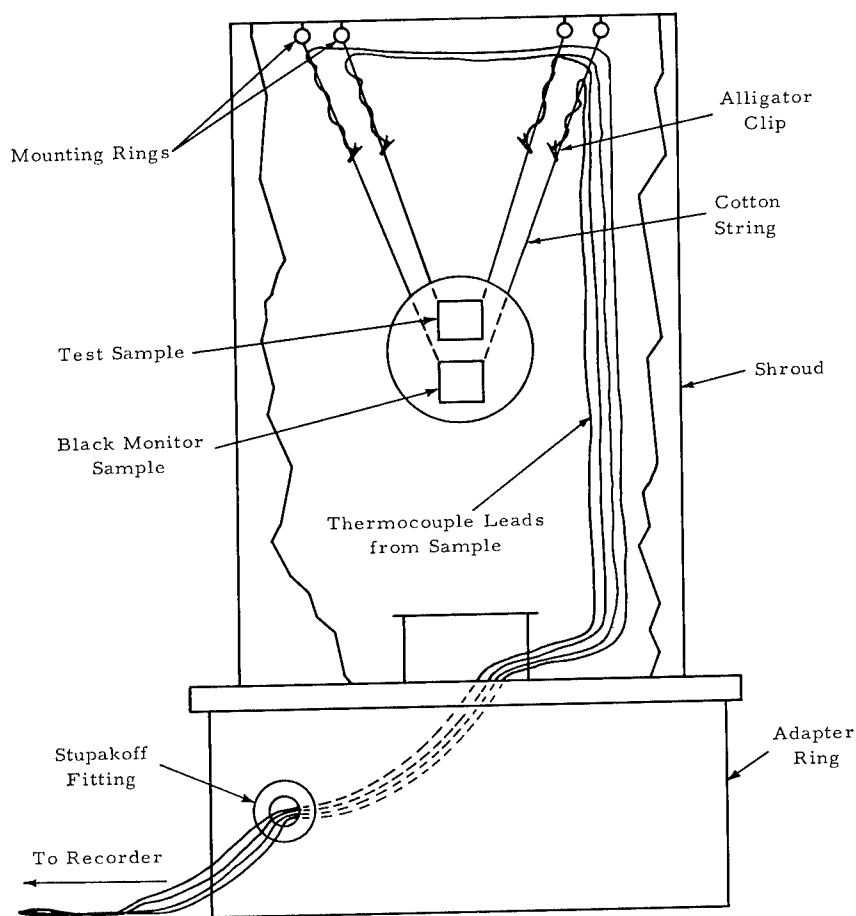
FIGURE 88.—Sample suspension technique and thermocouple vacuum feed-throughs.

ing equipment.   A fused-quartz lens is used to focus the light upon the sample within the chamber.   A light chopper is interposed between the vacuum chamber window and the simulated solar source to provide adjustment of the light intensity while allowing the arc to operate at optimum stability.

Test samples (fig. 87) are sandwich-constructed (2 inches square and ≈ ⅛ inch thick).   Samples are constructed with a jig to insure correct placement of the thermocouple lead wires.   Of particular importance is the assurance of good thermal contact between the thermocouple bead and the two copper plates.   This requirement is met by forcing the copper plates against the thermocouple.   The sample is mounted by supporting the sample and a reference sample opposite the sight port from the thermocouple lead wires (fig. 88).
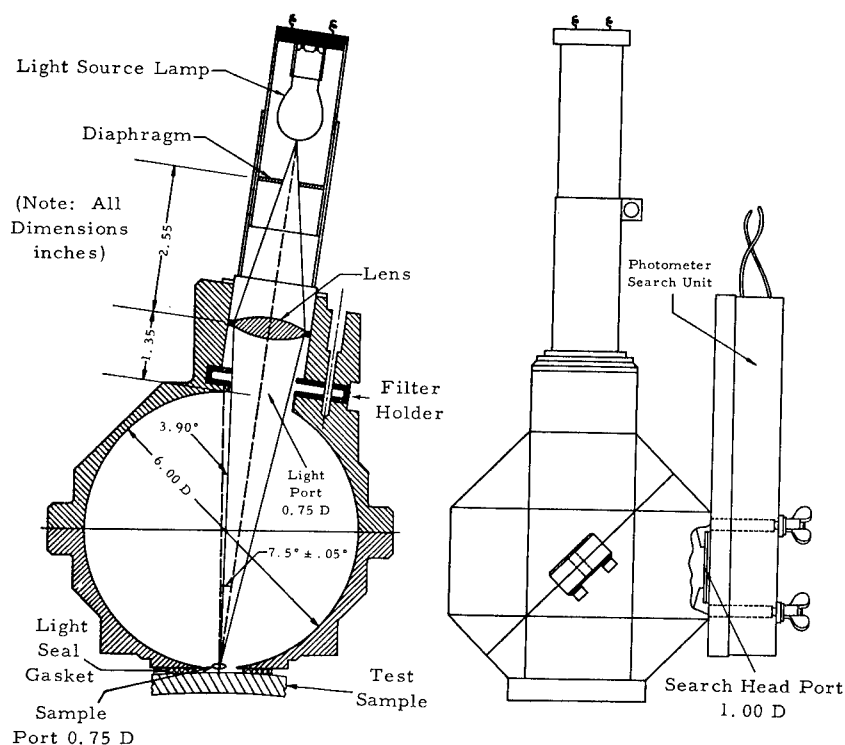
FIGURE 89.—Cross section of integrating sphere: "All dimensions in inches."

Measurements are made by evacuating the vacuum system to a pressure in the 10^{-7} Torr range, cooling down to -190 °C by admitting liquid nitrogen to the shroud, then starting the arc. When all three functions equilibrate, the moveable door is opened exposing the sample to the simulated solar source. The sample begins to heat from the thermal input, and after the desired temperature range is traversed the port is closed. Afterward, the sample cools by radiation. Both dynamic heating and cooling curves are recorded by multipoint recorders.

Errors associated with gas conduction, thermocouple wire conduction, and variation of sample specific heat with temperature were taken into account through analytical models. Data reduction procedures were developed and are described in detail. A comparison of results is given in table 31. Future improvements affecting various parts of the hardware, but not the principle of the method, were discussed.

REFLECTANCE MEASUREMENTS

Fussell, Triolo, and Jerozal (ref. 6), NASA Goddard Space Flight Center, developed a portable, integrating-sphere, reflectance apparatus

for field monitoring and quality control measurements of spacecraft coatings over the wavelength interval 0.27 to 1.65μ. This device is of great importance in the verification of the optical properties of spacecraft surfaces just before launch. The construction, testing, and mounting of a spacecraft on a launch vehicle is a tedious and time consuming task. It is not unusual for months to elapse between coating and launch. Under these circumstances even the most careful protection may not prevent surface contamination or soiling. In the case of organic finishes there is always the possibility that the warm and humid Florida climate will encourage an organism to develop an appetite for a particular coating. The salt air can corrode metal surfaces with unexpected rapidity. Thus, apparatus to measure optical properties is of particular importance.

The integrating-sphere coating monitor (fig. 89) consists of a light source, optics, and an integrating sphere with the sample port at the bottom. The side-mounted photomultiplier is monitored by a Photovolt Corporation model 520-M photometer supplied by a stabilized voltage. Photomultiplier tubes having S-1, S-4, S-5, and S-11 spectral sensitivity cathodes are available as accessories. The light source is a General

TABLE 31.—*Comparison of Solar Absorptance and Thermal Emittance Values, Obtained by Optical and Thermal Vacuum Measurements, for Four Common Spacecraft Coatings*

Coating*	α and ϵ Values†					
	$(\bar{\alpha}/\bar{\epsilon})_H$	$\bar{\epsilon}_{vc}$	$\bar{\epsilon}_{NC}$	$\bar{\epsilon}_{NM}$	$\bar{\alpha}_c$	$\bar{\alpha}_{DK}$
Evaporated Gold_____	9.2	0.0239	0.015	_____	0.195	0.200
Aluminized Mylar‡_____	2.68	0.0618	0.037	0.035	0.129	0.131
Evaporated Aluminum_____	4.02	0.0424	0.026	0.022	0.17	0.156
Carbon Black Paint, Silicon Vehicle.	1.18	0.817	0.872	0.907	0.964	0.956

* Vacuum-deposited metals, and paint.
† Where $(\bar{\alpha}/\bar{\epsilon})_H$ = ratio of solar absorptance to total normal emmittance (for T = 300° K),

$\bar{\epsilon}_{vc}$ = uncorrected total hemispherical emittance as measured thermally,

$\bar{\epsilon}_{NC}$ = corrected total normal emittance calculated from thermally measured total hemispherical emittance,

$\bar{\epsilon}_{NM}$ = total normal emittance measured optically (should be close to $\bar{\epsilon}_{NC}$),

$\bar{\alpha}_c$ = solar absorptance calculated from thermal measurements with a carbon arc solar simulator,

$\bar{\alpha}_{DK}$ = solar absorptance calculated from optical measurements (should be close to $\bar{\alpha}_c$).

‡ With scribed lines 2 to 3 mils thick forming ¼-inch squares of evaporated aluminum.

Electric No. 1493 microscope illuminator lamp. Stabile intensity was achieved by aging the lamps for one hour at the rated voltage and current (6–5v and 2.75a). A Harrison Laboratories model AX stabilized power supply regulating the output to 0.01 percent was found to be a suitable power supply for the lamp. The major components of the apparatus are shown in figure 90.

Measurements of opaque materials could be determined as a function of wavelength by the insertion of 2-inch square interference filters for spectral resolution. Reflectance of a sample was measured by comparison with a standard in a sequential manner. Readings were taken first of a standard, then of the sample, and finally a reading of the standard was made.

Complete operating directions, sources of error, and suggested improvements were discussed in detail. Short-term fluctuations were less than ±0.5 percent and the long term drift was ±2.8 percent per day. The error was estimated to be 4.4 percent at 0.4μ, 7.2 percent at 0.6μ, 6.5 percent at 0.8μ and 5.3 percent at 1.0μ for a standard having a 100 percent reflectance and a sample having 0 percent reflectance. The estimated overall accuracy is approximately ±20 percent or better.
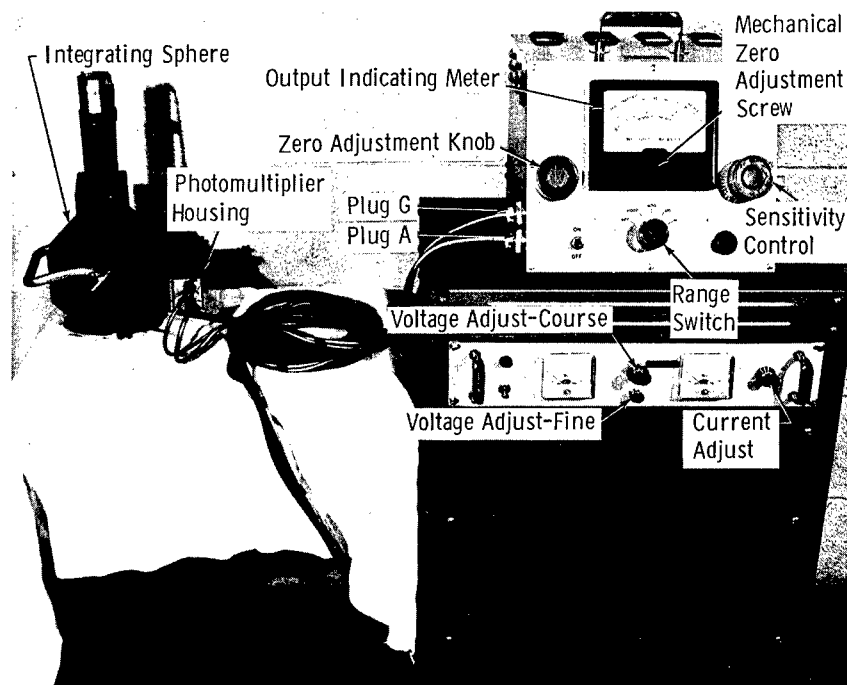
FIGURE 90.—Reflectance monitor panel components.

1-Specimen
2-Heater Tube, 5/8 O.D. 9/16 I.D. Inconel
3-Thermocouples
4-Voltage Leads to Measure Power to Specimen
5-Guard Heaters
6-Nicrome Heater Wire
7-Current Leads
*-Not Drawn to Scale
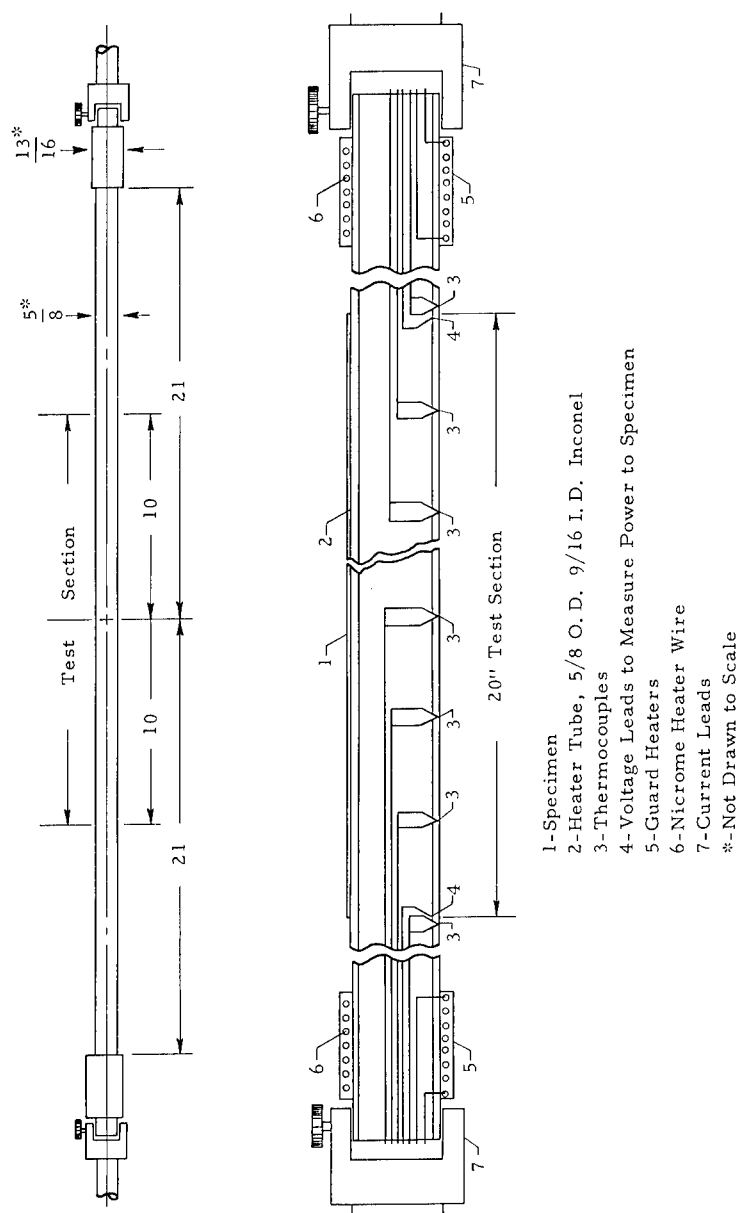
FIGURE 91.—Drawing of heater rod.

EMISSIVITY MEASUREMENTS

The classification of emissivity apparatus by temperature ranges follows the general outline of Richmond (ref. 1) with slight modifications. Though these ranges are to some extent arbitrary, nonetheless, when experimental techniques are reviewed on a large scale this approach is quite a workable one. To anyone seriously interested in the field of emissivity measurements, the symposium results edited by Richmond is "must" reading since it is more important than any other publication in the field. Also, since this work is available and contains several papers relating to NASA contributions, fewer details will be given to these NASA papers than have been given for some previous papers in this survey report.

LOW-TEMPERATURE RANGE (0–500° K)

Ward and McDonough (ref. 7), NASA Langley Research Center, perfected an emittance apparatus to measure the emittance of very thin sheet materials over the temperature range 0° to 100° C. This equipment consists of a tubular heater rod placed concentrically inside a liquid-nitrogen-cooled and internally-blackened outer chamber. The heater rod is shown in figure 91, and the wrapping of a sample onto the heater in preparation for insertion into the liquid nitrogen shroud is shown in figure 92.
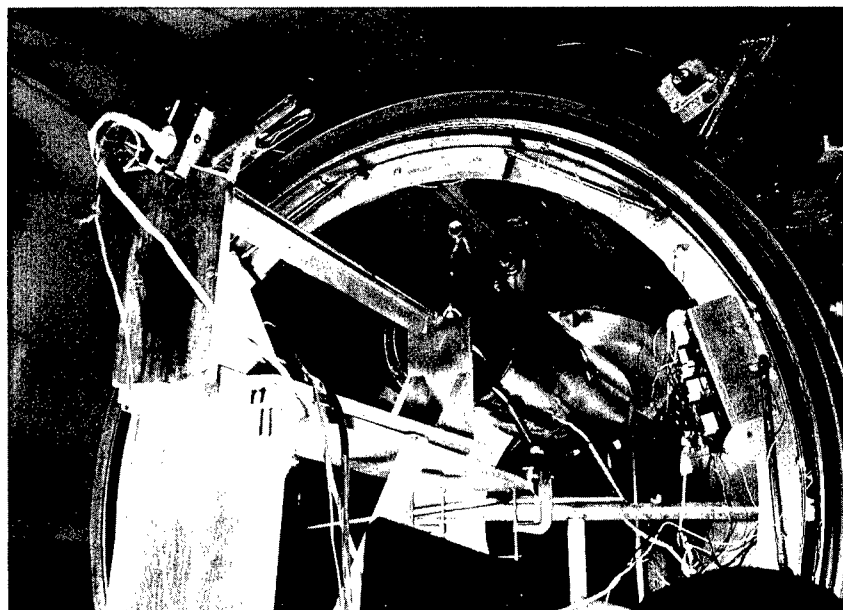
FIGURE 92.—Sample being wrapped onto the heater rod in preparation for insertion into the outer liquid nitrogen shroud.

Measurements were made by applying power to the heater rod with the main power supply (after the vacuum system was evacuated to a pressure of about 1×10^{-6} Torr) until the temperature reached the desired level. Thermocouples attached at the various points indicated the axial gradient on the interior of the heater tube. Power was supplied to each of the end guard heaters to bring the sample to a uniform temperature. In this condition the power applied to the center section was equal to the power emitted. The power was measured by determining the voltage drop along a specified sample length and measuring the current flow. About 5 hr was required to evacuate the system and measure three points at different temperatures.

This apparatus has an estimated overall maximum error of less than 6 percent and is particularly useful for measuring sheet materials when large samples are required.

Zerlaut (ref. 8) developed an apparatus whose general construction follows that developed by Wilkes (ref. 9). The details of the device are shown in figure 93. Essentially a blackbody and a sample are heated to identical temperatures and alternately presented to the view of a radiometer. The difference in signals gives a first approximation of the emissivity of the sample. Zerlaut provides details of operation, methods of thermopile calibration, a discussion of numerous problems encountered, and a general discussion of results obtained. This apparatus is useful for screening of materials over the temperature range at and above room temperature. It is not useful at lower temperatures and requires modification for elevated temperature measurements.

INTERMEDIATE-TEMPERATURE RANGE (500–1500° K)

Askwyth, Curry, and Lundberg (ref. 10), working under NASA Contract at the Pratt and Whitney Aircraft Division of United Aircraft Corporation, designed a novel apparatus. This method is based on the principle that if fins, identical in every respect except emittance, are heated at one end to the same temperature and in the same environment, the temperature gradient along the length of the fin is a function of emittance only. Apparatus was constructed using this principle and aluminum fins were coated with different coatings of unknown emissivity. A comparison of the temperature drop along fins with different coatings indicated reasonable experimental agreement. An analysis of the fin parameters was made and indicates that the apparatus is useful in principle over the temperature span $-100°$ F to $1,350°$ F. This method does not allow a good determination of the emissivity temperature coefficient, and in fact has little to recommend it over more standard techniques.

Greenberg (ref. 11), NASA Lewis Research Center, has developed apparatus for measuring the absorption spectra of salts above and below
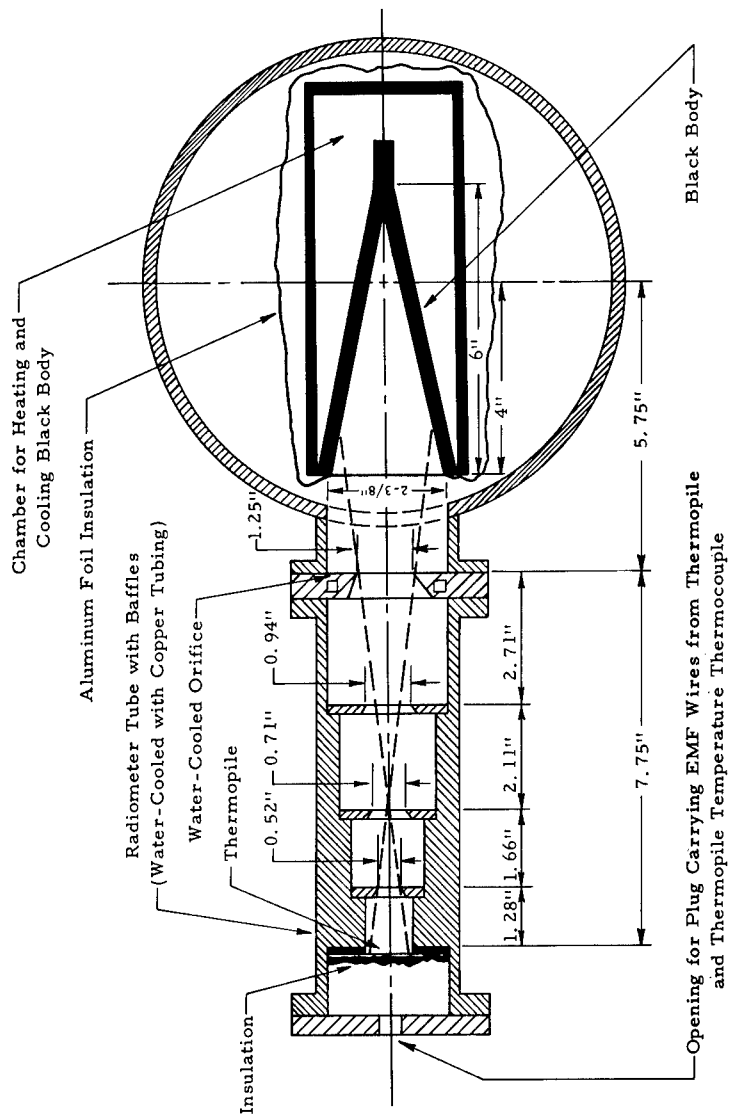
Figure 93.—Top view section of emissometer with blackbody in position.
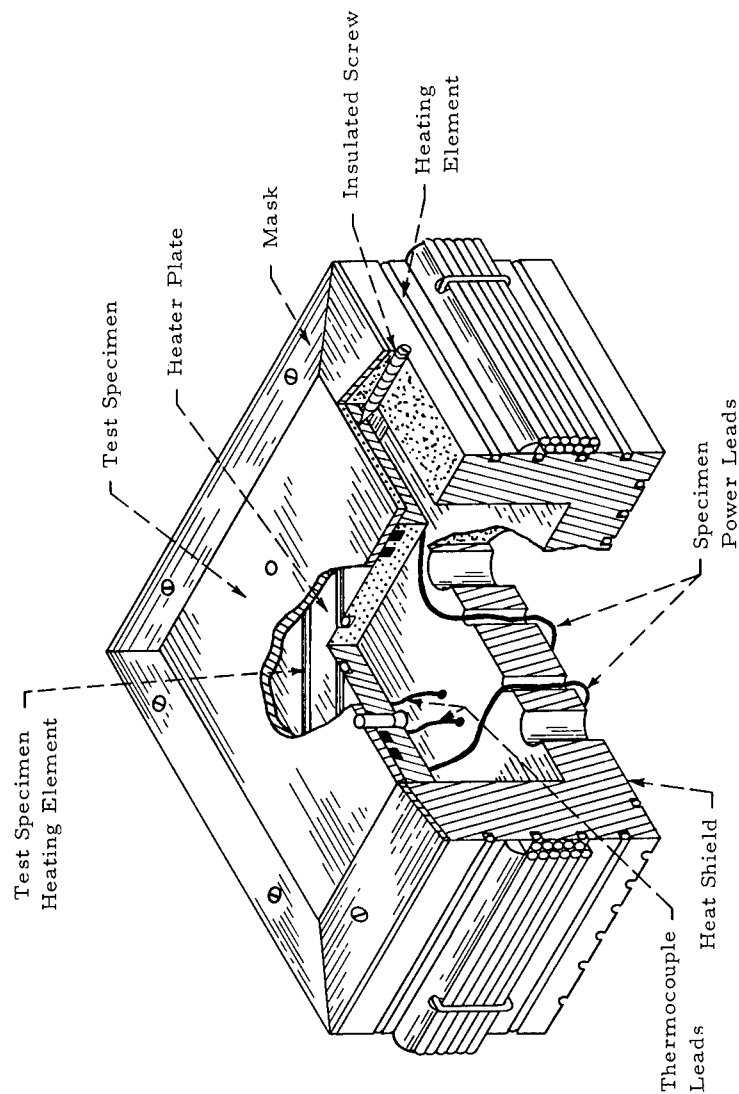
FIGURE 94.—Test specimen mounting assembly.

their melting points in the near ultraviolet, visible, and near infrared with a modified Beckman D. V. spectrophotometer. This equipment makes use of fused silica sample cells of special design. Emission and reflectance spectra were also measured. In general, the problems associated with the measurement of the optical properties of molten salts arise from the reactivity of these salts with most optical-window materials. Data are presented for inorganic materials. This device is of significance to inorganic coatings because some coatings will probably be required to operate at temperatures above their melting points.

Nyland (ref. 12) developed a steady-state, heat-balance method which is useful for determining the total hemispherical emittance, solar absorptance, and the ratio of solar absorptance to emittance. A sample holder is illustrated in figure 94. The assembled unit shown in figure 95 is ready for insertion into the vacuum chamber. For a determination the sample is placed in an evacuated vacuum chamber and various optical measurements are made. The sample is surrounded by a blackened surface, liquid nitrogen shroud for hemispherical emissivity measurements and a heated shroud for high temperature absorptance tests. A guard heater surrounds the sample on the back face and on the edges, and is controlled by a set-point automatic temperature system which is described in detail. For (α/ϵ) ratio measurements a commercial carbon arc simulated solar source is used.

A detailed error analysis was made which considered both systematic and random errors. The error summary indicates that measured values should range between 2.1 percent higher and 4.0 percent lower than the
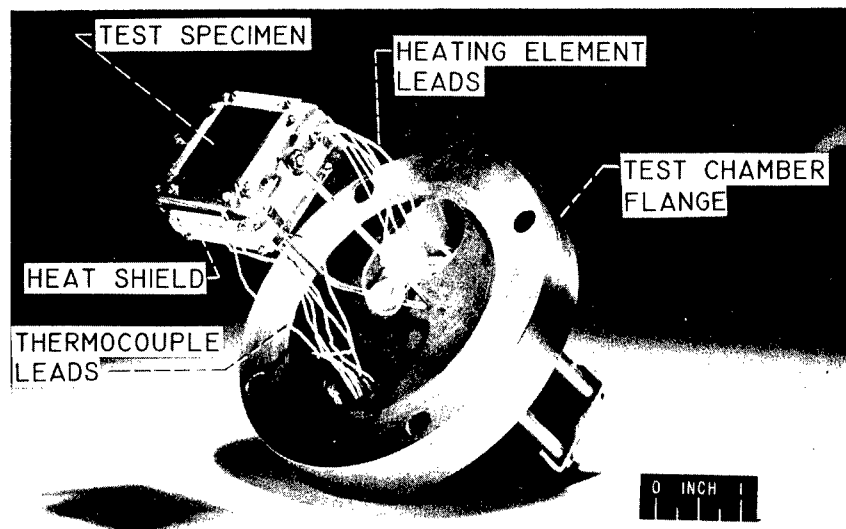
FIGURE 95.—Test specimen mounting assembly with flange.
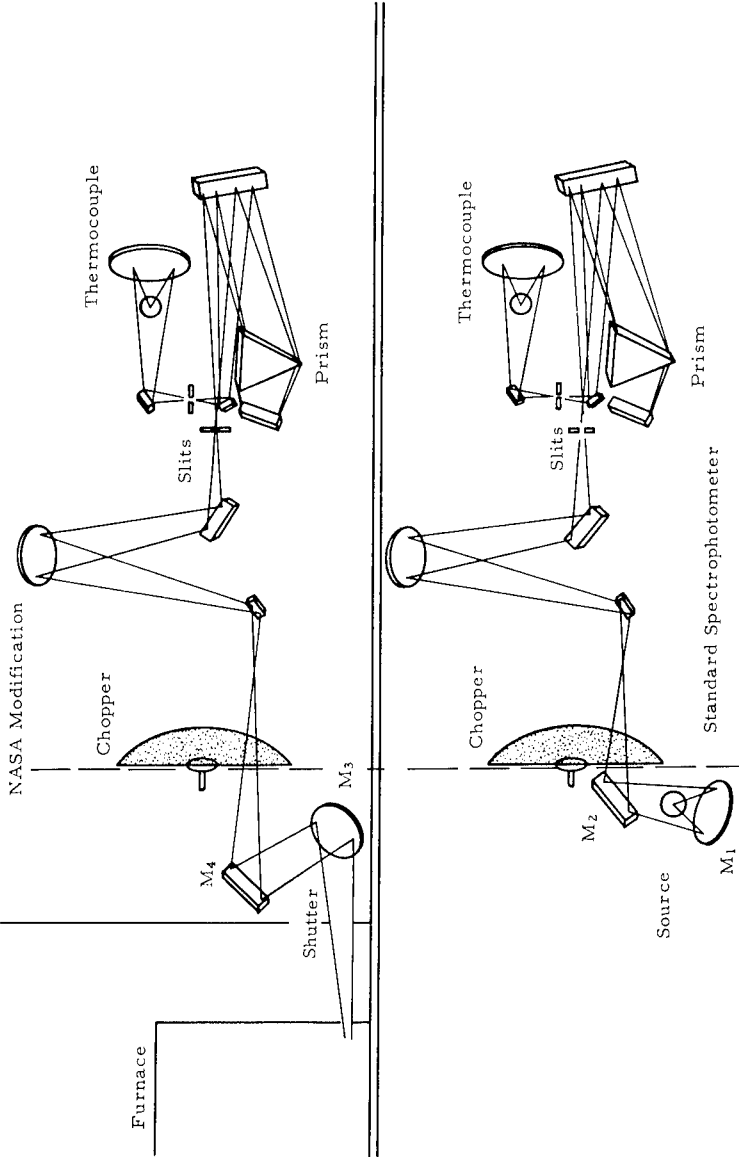
FIGURE 96.—Optical schematic of spectrophotometer.

measured emittance with variations of less than 0.01.   Repeatability of emittance measurements has been found to be about ±2 percent.

Slemp and Wade (ref. 13) described an emittance apparatus based on the general concept set forth by McMahon (ref. 14).   The apparatus consists of two parts: a blackbody furnace holding the sample, and a spectrophotometer for measuring the spectral emissivity from 1.0 to 15.0μ.   The optics were altered as diagrammed in figure 96 to allow the use of an external source.   A cover was designed which permitted a water cooled shutter to exclude the external source as desired.

The furnace consists of an inner, heavily oxidized liner to serve as a blackbody cavity of uniform temperature, surrounded by a silicon carbide cube wound with 17-gauge Nichrome V resistance wire.   The silicon carbide shell is insulated to reduce power requirements.   The lower half
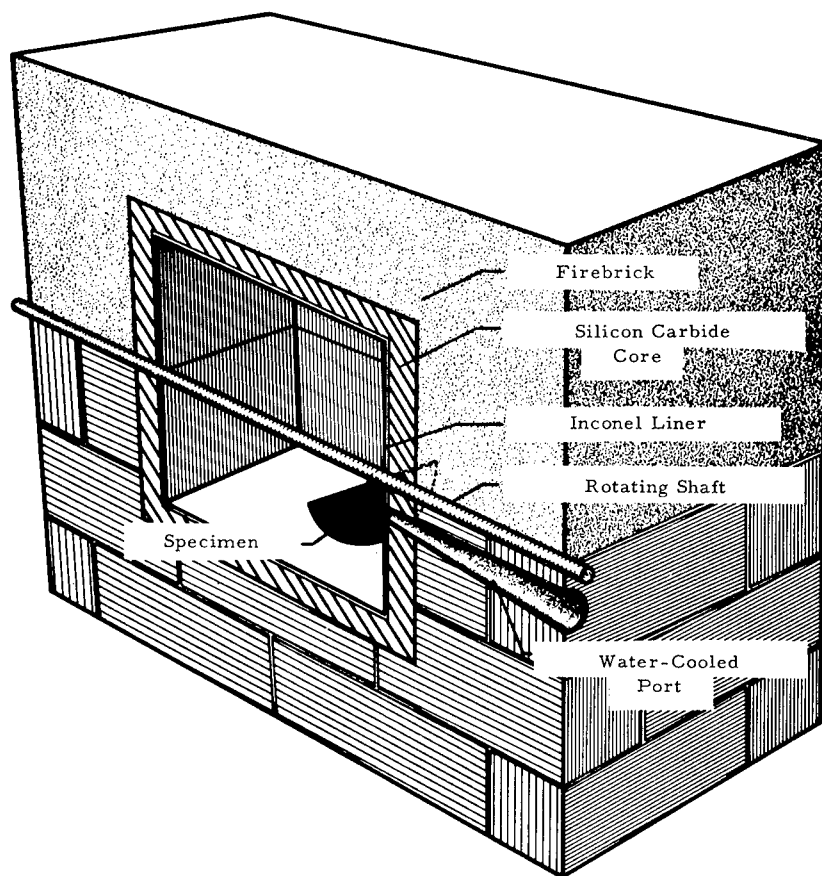
FIGURE 97.—Cross section of blackbody furnace.

$$\epsilon_{\eta\lambda} = \frac{V_s - V_o}{V_B - V_o}$$
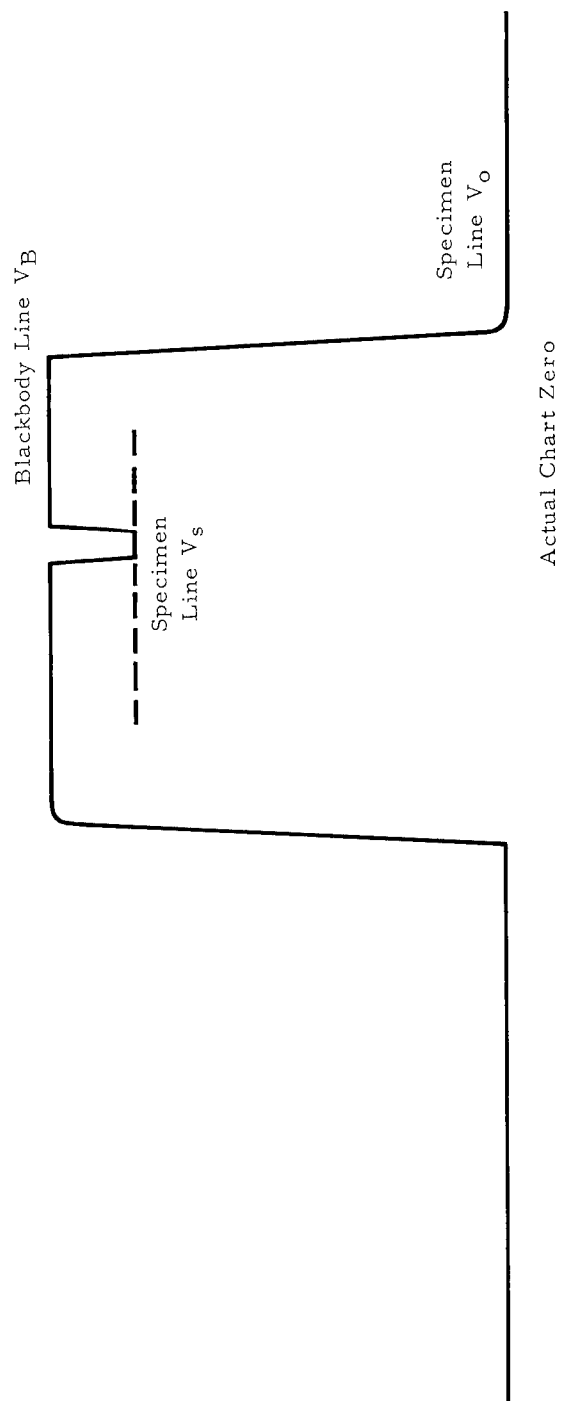
FIGURE 98.—Typical data trace.

⊙ BLAU et al. at 760°C

▢ NASA Data at 810°C

Wavelength (Microns)

Spectral Normal Emittance
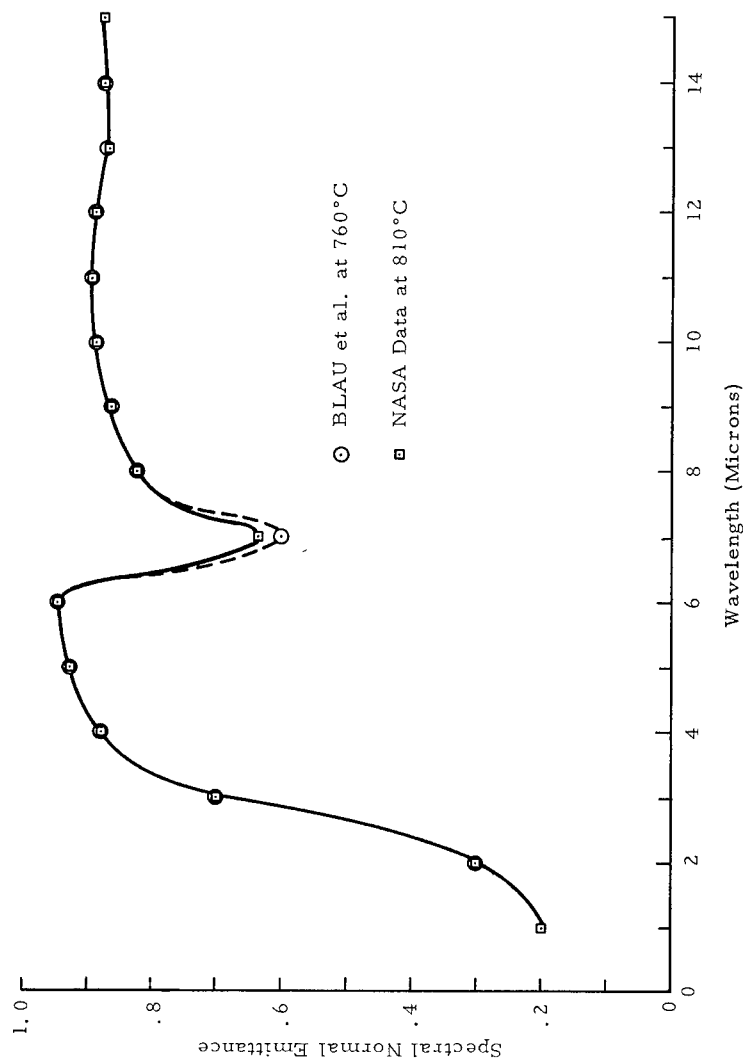
FIGURE 99.—Boron nitride.
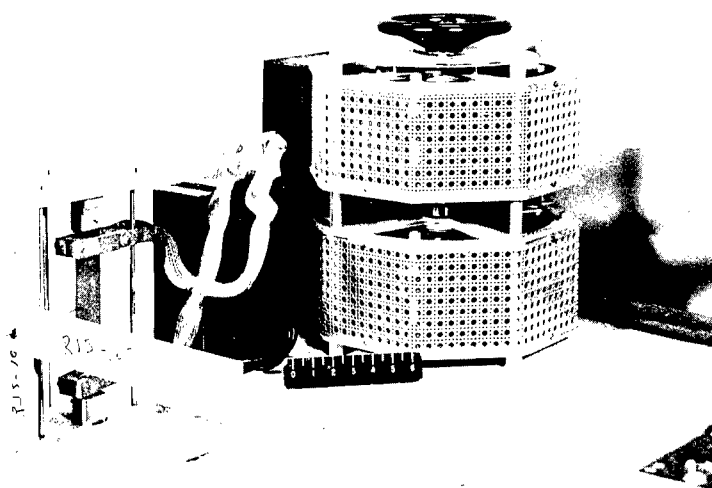
FIGURE 100.—Emittance specimen and power supply.
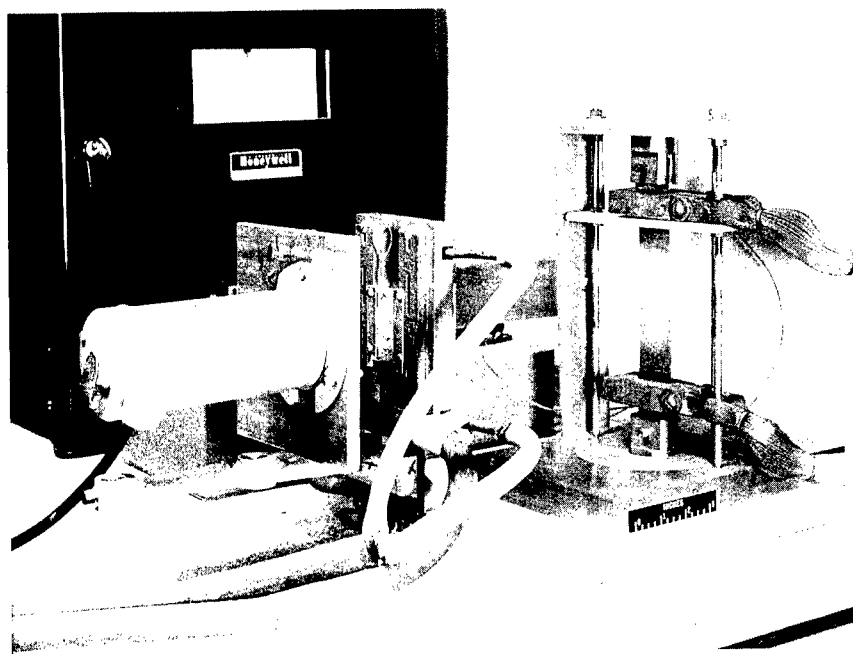
FIGURE 101.—Thermopile and water-cooled shield mounted on pivoted arm of test specimen holder with test specimen installed.

of the furnace contains a water-cooled, sight port which extends up to within $\frac{1}{16}$ inch of the front surface of a flat sample which is rotated by a 15 rpm motor past the viewing port. The furnace is capable of continuous operation at 1,900° F (fig. 97).

The test procedure is simple and consists of mounting $\frac{1}{8}$-inch thick semicircles of 4-inch diameter on the rotating shaft. After temperature equilibrium is attained the sample is rotated past the spectrometer beam giving three intensity values. A typical data trace is shown in figure 98. The total error is estimated to be less than 5.0 percent. The reproducibility was determined to be 0.5 percent.

The major advantage of this system is that it does not require thermocouples to be attached to the samples. Materials which are not opaque must use the more complicated expressions of McMahon (ref. 14) to calculate emittance, but they can be measured successfully. For samples of low conductivity the temperature drop of the surface can be a significant source of error. However, the equations of Peavy and Eubanks (ref. 15) can be used to estimate rather accurately the errors associated with this temperature drop with rotation. The results shown for boron nitride in figure 99 compare quite closely with data taken by Blau, Marsh, Martin, Jasperse, and Chaffee (ref. 16). This method appears very useful for measuring the normal spectral emittance of solids and coatings over the temperature range 800° F to 1,800° F and the wavelength region
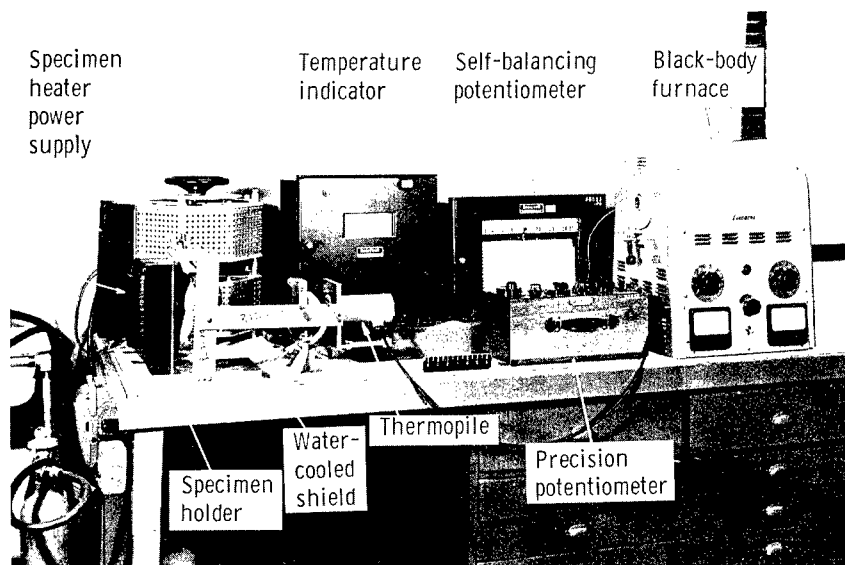
FIGURE 102.—General view of emissivity-measuring apparatus with identification of principal components.

1.0μ to 15.0μ. The wavelength range is not limited by the furnace design, but by the spectrophotometer prism and detector. A blackbody furnace similar in design has been constructed with platinum windings to allow measurements of emittance at temperatures up to 2,500° F.

O'Sullivan and Wade (ref. 17) developed a useful apparatus for measuring the normal emittance of coated and uncoated metals over the temperature range 600 to 2,000° F for most conductors. In addition, the angular-distribution of emitted energy can be determined for angles up to 60° from the normal. The sample consists of a flat strip specimen held between end chucks (fig. 100). A stepdown transformer and a variable voltage transformer supply power to heat the specimen. The sample temperature is measured by a thin thermocouple bead attached to the midpoint of the sample. The radiation temperature of the specimen is determined by a radiometer sighted upon the midpoint of the sample as shown in figure 101. The complete emittance apparatus is presented in figure 102, with the various parts identified. The blackbody-furnace contains a conical blackbody equipped with a thermocouple as shown in figure 103. This blackbody-reference cavity is required to calibrate the thermopile.
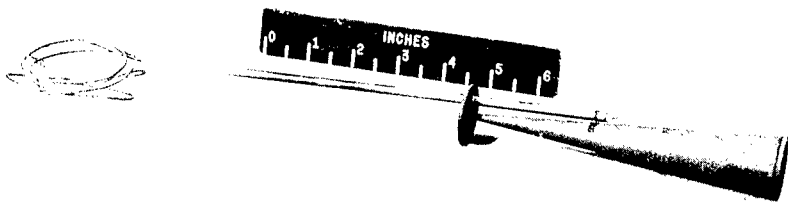
FIGURE 103.—Reference blackbody conical target with thermocouple.

This apparatus is simple in design and requires samples which are easily fabricated. However, it is a useful and accurate method of obtaining emittances. O'Sullivan and Wade gave a detailed treatment of the theory of operation of the apparatus. This apparatus has also been used by Wade and Casey (ref. 18), NASA Langley Research Center, to measure total emittances of several oxidized, nickel-titanium, carbide-cemented materials; and by Wade and Slemp (ref. 19), NASA Langley Research Center, for total normal emittance measurements of several refractory oxides, cements, and ceramics up to 2,000° F.

HIGH-TEMPERATURE RANGE (1500° K AND UP)

Wilson (ref. 20), NASA Langley Research Center, has recently presented some initial results obtained with an emittance apparatus useful for determining spectral emittance and reflectance of refractory solids to 6,000° F. This equipment uses a carbon arc source and two imaging mirrors. Basically the apparatus is similar in principle to that developed by Null and Lozier (ref. 21). Wilson details the apparatus, test methods, and temperature measurement methods used in connection with this apparatus. Data is presented for the spectral emittance and reflectance of carbon, graphite, and zirconia samples of different surface roughnesses for temperatures up to 5,200° F. This apparatus should be useful in determining the emissive properties of coatings at very high temperatures, though there is uncertainty connected with the effects due to non-uniform temperature distributions present in semitransparent materials.

OPTICAL MEASUREMENTS STANDARDIZATION

After discussions between Mr. Carr Neel, NASA Ames Research Center, and Mr. William Carroll, NASA Jet Propulsion Laboratory, the need for a voluntary round-robin test series became evident. This program was designed to allow each investigator the maximum freedom in making measurements to obtain as broad a spectrum of methods, procedures, and apparatus as possible in studying carefully standardized samples. Measurements of optical properties were to be (if possible): (1) solar absorptivity (α), and (2) hemispherical emittance (ϵ). Samples were to be exposed to vacuum ultraviolet irradiation for optical properties alteration due to degradation. Therefore, the program was designed to intercompare optical measurements and optical degradation testing procedures. Furthermore, this round-robin test program was planned to use samples that will be included in the OSO–B flight making possible a valuable cross check with space exposure data. Mr. Carr Neel, program administrator, supplied the following information.

PURPOSES

1. Intercomparison of laboratory data.
2. Intercomparison of methods of predicting behavior in space from laboratory data.
3. Intercomparison of predicted behavior with flight data when this becomes available from the surface experiment on S–17 (OSO–B).
4. Development of reliable methods for predicting behavior of thermal control surfaces in space.

SURFACES

1. The two degradable materials included in the program are:
   a. Virtually opaque samples of white Skypar (A423 color SA 9185

untinted) a TiO$_2$-pigmented epoxy base paint (A. Brown). Substrate $\frac{1}{16}$ inch thick, $\frac{15}{16}$ inch diameter 6061 aluminum alloy discs, prepared by LMSC (L. A. McKellar).

   b. Virtually opaque samples of antimony oxide-pigmented potassium silicate base paint. Substrate 15-inch diameter aluminum discs, prepared by HAC (G. R. Blair).

2. Additional materials available for evaluation, if desired:

   a. One of the "stable" white coatings which will also be included in the OSO–B experiment.

   b. Samples of the same composition as the Rutile-Silicone paint which was used on the OSO I experiment. (Preliminary flight data on this material will be available from the OSO I experiment. However, these samples will not be prepared from the same lots of material as the flight samples.)

PROCEDURE

1. Issue letter requesting participation to:

     Mr. Carr Neel

     Ames Research Center

     National Aeronautics and Space Administration

     Moffett Field, California

   Indicate:

   a. Samples required.

   b. Reservation or exceptions to participation.

   c. Anticipated completion date (approximate).

2. Samples will be distributed by Mr. Neel.

3. Perform tests and reduce data (for information required see Solid Lubrication Coating).

4. Prepare sufficient copies of full data for all participants (approximately 15–20 copies); transmit to Mr. Neel.

5. Mr. Neel will send copies of all data to all participants, along with a list of participating recipients.

6. A terminal meeting of participants will be held to discuss results. (Approximately March 1, 1964, or sooner, if possible.)

7. Flight data from OSO–B will be forwarded to participants as soon as available.

DATA REQUESTED

1. Exposures

   a. Required: three samples of each of two materials, preferably at different total exposures.

   b. Preferred: nine separate runs per material, if possible.

   c. Decade spent in total exposure, if possible (i.e., 100 hours and 1,000 hours; 50 hours and 500 hours, etc.).

   d. Total exposure should be within range of 5 to 1,000 "sun hours."

    e. Intensity (acceleration) and total dose at the option of each individual investigator.
2. Exposure information
    a. Brief description of equipment.
       (1) Ultraviolet source
          (a) type of ultraviolet source used
          (b) distance from sample—if different distances are used, identify distance with results of individual tests
          (c) window or other absorbing medium between source and sample
          (d) lamp age
          (e) method of monitoring during test; include data, if available
       (2) Environment
          (a) vacuum level or atmosphere
          (b) type of vacuum equipment
    b. Definition of one "sun" ultraviolet and method of calculation (or total energy per unit area and defined wavelength band). Include spectrum of source, if possible.
    c. Sample temperature.
       (1) Type and location of measurement
       (2) Sample cooling
3. Data
    a. Spectral plots of α vs. λ, overlaid, if possible, with exposure as a parameter.
    b. Plot α_s or $\Delta\lambda_s$ vs. total sun hours $< 4000\overset{\circ}{\text{A}}$.
    c. Plot α_s or $\Delta\lambda_s$ vs. total sun hours by your normal comparison procedure. (Specify method—see 2–a–(2), above.)
4. Related information.
    a. Time interval between termination of test and measurement of $\alpha\lambda$; any important facts about storage or transport of samples from test apparatus to measurement device.
    b. Accuracy of a determination.
    c. (When not testing samples, before tests, keep covered to avoid any deterioration by natural sunlight or fluorescent lamps.) If exposed for more than 12 hr total, report the time exposed (approximate hours).
Note: The items listed are all considered to have an important effect on test results and should be included to aid analysis of results.

PARTICIPANTS IN ROUND-ROBIN

1. Space Technology Laboratories
One Space Park
Redondo Beach, California

Attn: Mr. J. T. Bevans

2. The Boeing Company
   Aero-Space Division
   Seattle, Washington
   Attn: Mr. R. J. Tallent—Mail stop 41–17

3. American Cyanamid Company
   Central Research Division
   1937 West Main Street
   Stanford, Connecticut
   Attn: Dr. Norma Searle

4. Hughes Aircraft Company
   Florence at Teale Street
   Culver City, California
   Attn: Mr. G. R. Blair—MSD–133

5. Lockheed Missiles and Space Corporation
   3251 Hanover Road
   Palo Alto, California
   Attn: Mr. L. A. McKellar—Dept. 52–20, Box 204

6. Marshall Space Flight Center—NASA
   Huntsville, Alabama
   Attn: Dr. W. R. Lucas
   Chief of Engineering, Materials Branch

7. Langley Research Center—NASA
   Langley Field, Virginia
   Attn: Dr. George F. Pezdirtz
   Spacecraft Materials Section
   Space Vehicle Branch—Building 1251

8. ASRC NE–2
   Air Force Materials Laboratory
   Wright-Patterson Air Force Base, Ohio
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9. U.S. Naval Research Laboratory
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   Washington, D.C.
   Attn: Mr. D. E. Field
   Chemistry Division

10. General Dynamics—Astronautics
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    Attn: Mr. W. Claussen

11. General Electric MSVD
    Space Science Laboratory
    Valley Forge, Pennsylvania
    Attn: Mr. Charles Foster

12. Jet Propulsion Laboratory
    4800 Oak Grove Drive
    Pasadena, California
    Attn: Mr. W. F. Carroll
13. ITT Research Institute
    10 West 35th Street
    Chicago 16, Illinois
    Attn: Mr. G. A. Zerlaut
14. McDonnell Aircraft Corporation
    P.O. Box 516
    St. Louis, Missouri
    Attn: Mr. E. T. Kisselburg
15. Martin-Marietta Corporation
    Denver Division
    P.O. Box 179—Attn: Mr. Larry Schlenker
    Denver, Colorado—Mail No. L8
16. Fairchild Aircraft Company
    Hagerstown, Maryland
    Attn: Mr. S. Dennis Farnsworth
    Chief, Materials Technical Laboratories
    Department 136

The preliminary results of this test series were reported by Arvesen, Neel, and Shaw (ref. 22), NASA Ames Research Center. Due to the importance of this report, the abstract is reproduced here.

ABSTRACT

Comparisons of laboratory results of ultraviolet degradation of thermal control coatings for spacecraft with data obtained during flight-in-space have shown generally poor agreement in the rate of coating degradation. Consequently, it has become apparent that improvements must be made in laboratory ultraviolet-simulation techniques. In November, 1962, a round-robin testing program was organized in an attempt to advance the technology of ultraviolet testing of thermal control coatings. In this program, samples of four different temperature control coatings were distributed among a number of organizations for tests in their ultraviolet-simulation facilities. Sixteen organizations are participating in the program. Three of the coatings were known to be unstable when exposed to ultraviolet, whereas the fourth was considered to be relatively stable. The stable coating and two of the unstable samples have been included in the complement of test coatings for the flight emissivity experiment on the S–17 Orbiting Solar Observatory. The results from this experiment should provide a basis for evaluating the capability of the various laboratory facilities to simulate the degrading effects of solar ultraviolet radiation.

The information presented is based on a preliminary analysis of the results reported by approximately half of the participants. The rate of increase in solar absorptance of the test coatings varied widely among the different investigators. For example, the rate of degradation of samples of one of the coatings was found to differ by factors exceeding 50. In addition, initial values of solar absorptance for the same coatings were found to differ in some cases by nearly 100 percent.

Preliminary analysis of the results obtained from this program illustrates the need to standardize test techniques for ultraviolet degradation studies and to obtain correlations of laboratory measurements with data taken during flight in actual space environment. It is also evident that standardization of measurement techniques for determining thermal radiation properties is required.

COMMERCIAL IMPLICATIONS

The NASA contributions have been and are a major source of progress in the technology of optical property measurements. The growing level of taste and visual sensitivity of an increasingly well educated public will be reflected in the demand for better designed color systems used in the commercial economy. The improvement in optical measurement apparatus will be available when required. This is not to indicate that NASA has designed or perfected apparatus of this type. It has not. On the other hand, the increase in technical capability of our society in the area of optical measurements has been a direct result of NASA contributions.

One product used by the space/missile industry has been designed and is being sold as a commercial product. Dynatech Corporation, 17 Tudor Street, Cambridge, Massachusetts, has developed a modified copy of the NASA dynamic (α/ϵ) apparatus and is marketing this device. The Thermo-Physics Corporation, 639 Massachusetts Avenue, Cambridge 39, Massachusetts, is currently designing apparatus based on the same NASA design for the measurement of solar absorptivity, emissivity and (α/ϵ) ratio measurements.

The portable reflection apparatus may very well have a market potential in the commercial economy for quality assurance of surfaces in situ. For example, the construction industry could use it to test both interior and exterior surfaces for specification inspection. The weathering of exterior building surfaces can be monitored over a period of time using this device, and this could encourage the development of surfaces with long term specifications with respect to optical property alterations. The Thermo-Physics Corporation is actively studying the NASA apparatus to redesign it as a prototype for a commercial device to fill this potential market.

Progress in the field of thermal radiation measurements, theory, and applications will ensue from the NASA/ASD/NBS jointly supported "Symposium on Thermal Radiation of Solids." It is impossible to predict or even fully understand at present the implications of the numerous commercial possibilities for the subdivision of technology. However, because heated objects radiate, the development of special heating equipment and the control of thermal losses are only two general areas wherein important commercial developments can be expected.

Refractory Metal Oxidation Resistant Coatings

The major advantage of refractory metals for structural applications is the retention of useful tensile strengths above 2,500° F (ref. 1). The major disadvantage is the catastrophic oxidation of refractory metals in air at temperatures above 1,500° F. Therefore, to utilize the desirable mechanical properties of this important group of materials for applications in the presence of the atmosphere, oxidation coatings are a necessity. Major development efforts have been pursued by the Air Force to meet specific current program requirements (ref. 2). NASA requirements for hot structures on re-entry spacecraft will not become pressing for some years yet; consequently, very limited funding has been expended in the evaluation of protective coating properties and failure mechanisms.

The actual production and application of current silicide, aluminide, and oxide protective coatings are primarily an art. One must admire the technical developments which have been achieved to date with so little fundamental scientific information. For example, many current coatings were developed without fundamental thermochemical or reaction-rate data. On the other hand it is to be expected that development progress cannot continue until the gap of fundamental information is bridged. NASA programs are designed to meet this need; however, budget limitations have prevented the program from achieving the momentum required.

COATING DEVELOPMENTS

Wakelyn (ref. 3), NASA Langley Research Center, developed a coating of vapor-deposited titanium nitride for the high-temperature protection of graphite from air oxidation. Graphite specimens of a cylindrical shape and capped with a hemispherical end ($\frac{3}{4}$-inch by $\frac{3}{8}$-inch diameter) were coated with TiN by the following reaction at 2,185° F:

$$TiCl_4 + 2H_2 + 1/2N_2 \rightarrow TiN + 4HCl$$
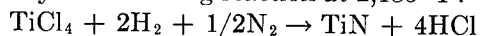
Ordinary tank-hydrogen containing nitrogen as an impurity was bubbled through liquid $TiCl_4$ and flowed over the heated graphite substrate.

Testing and evaluation were performed by heating coated and uncoated specimens in a Mach 2, 105 psi, 3,500° F air jet. Surface temperatures

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of the samples were monitored with an optical pyrometer.   During a 60-second exposure to the preheated air jet, the coated sample temperature reached 2,600° F and the uncoated specimen attained a temperature of 3,500° F.   Uncoated samples were completely oxidized.   Graphite specimens coated with a TiN coating greater than 20 mg/cm^2 were completely protected.   Thinner coatings were unsatisfactory.

The protection mechanism appears to be the formation of titanium dioxide which was detected on the surface of exposed samples, but not unexposed specimens.   While it is unlikely that a long life, high-temperature, oxidation-resistant coating will be developed based upon the titanium system since TiO_2 is not a particularly refractory oxide, the concept appears interesting as a method of obtaining tightly-bonded, nonporous coatings of the other two Group IV transition metal oxides, zirconia and hafnia.

Bliton, Christian, Harada, and Rechter (ref. 4) reported on the development of plasma-spread coating to protect tungsten above 3,500° F from oxidation.   This work is being sponsored by NASA under contract NAS 7–113.   The objective of this program is to produce tungsten rocket nozzles for low-pressure, liquid engines with test coatings.   The coating design consists of an outer 10-mil layer of oxide over layers of 60 percent oxide-40 percent tungsten (6 mils), a 40 percent oxide-60 percent tungsten (1 to 3 mils), and a $\frac{1}{16}$-inch tungsten shell.   The first oxide layer adjacent to the substrate contained 6–8μ tungsten particles, the second layer contained 37–44μ tungsten particles deposited using a power setting sufficient to produce only partly deformed particles which form a mechanical tie between the coating and the tungsten shell.   All oxide particles were between 10 and 25μ diameter.   Studies are to be conducted with hafnia and 50 percent hafnia-50 percent strontium zirconate coatings. No test results are currently available.

HIGH TEMPERATURE TESTING OF COATINGS

Trout (ref. 5) investigated the effects of a 60-sec exposure of various coated and uncoated refractory materials to a Mach 2.0, 3,800° F, 105 psi stagnation pressure air stream.   Photographic studies were made before, during, and after the erosion process.   The samples tested were 3 inches long, by $\frac{1}{2}$-inch diameter, hollow tubes closed on the end with hemispherical caps.   A second sample, $1\frac{1}{4}$-inches × $\frac{3}{4}$-inch diameter and hemispherically ended, was screwed onto a mounting shaft for testing.

The complete results are tabulated in tables 32 and 33.   Under the test conditions models of molybdenum containing 0.5 percent titanium were successfully protected against oxidation by chrome-plate, chromalloy W–2, nickel aluminide, flame-sprayed molybdenum laminate, and flame-sprayed alumina-molybdenum laminate.   Unprotected molyb-

TABLE 32.—*Description of Models and Tests*

Description of material	Model configuration	Photographs of model	Figure	Duration of test, sec	Reaction of model during test	Remarks
Molybdenum, unprotected	1	Before and after test. During test	4(a) 4(b)	26	Oxidation rate increased with surface temperature, ignition occurred at about 26 sec.	
Molybdenum, electroplated with 3 mils of nickel undercoat and 2 mils chromium electroplated on surface.	1	Before and after test. During test	5(a) 5(b)	59	Nickel and chrome plate failed progressively during test.	Exposed molybdenum did not ignite during test.
Molybdenum, coated with Chromalloy W–2.	1	Before and after test. During test	6(a) 6(b)	59	No failure occurred, surface blackened, slight flow of material on front face	
Same as previous test except ½-inch hole drilled ½ inch deep on center of front face of model.	1	During test	6(c)	60	Slight oxidation of material in drilled hole coating intact at end of test	Same appearance as model in previous test.
Molybdenum, electroplated with 4 mils of chromium.	1	Before and after test. During test	7(a) 7(b)	60	No failure of plating, surface blackened	Only 40 sec of film taken during test
Molybdenum, coated with 5 mils of nickel aluminide.	1	Before and after test. During test	8(a) 8(b)	58	No failure occurred, surface was blistered and darkened after test	
Molybdenum, coated with flame-sprayed molybdenum disilicide	1	Before and after test. During test	9(a) 9(b)	57	Model remained intact, surface darkened	

TABLE 32 (Continued).—Description of Models and Tests

Description of material	Model configuration	Photographs of model	Figure	Duration of test, sec	Reaction of model during test	Remarks
Molybdenum, coated with alternate layers of flame-sprayed zirconia and molybdenum, 3 layers of zirconia and 3 layers of molybdenum.	1	Before and after test. During test	10(a) 10(b)	58	Coatings failed progressively	Very little mass loss occurred on the exposed molybdenum surface
Molybdenum, coated with alternate layers of flame-sprayed alumina and molybdenum, 3 layers of molybdenum and 3 layers of alumina.	1	Before and after test. During test	11(a) 11(b)		Coatings failed progressively	
Tungsten, electroplated with 3 mils of nickel and 2 mils chromium electrodeposited on surface.	1	Before and after test. During test	12(a) 12(b)	p	Failure of plating produced rapid oxidation of tungsten	
Phosphate-bonded alumina chromia ceramic reinforced with spirally wrapped molybdenum wire.	1	Before and after test. During test	13(a) 13(b)	60	Surface spalled causing partial damage	
Hot pressed zirconium boride.	2	Before and after test. During test	14(a) 14(b)	60	Model intact after test	
Hot pressed siliconized boron machined after pressing.	2	Before and after test. During test	15(a) 15(b)	60	Some spalling of unfinished wall	
Hot pressed titanium boride machined after pressing.	1	Before test. During test	16(b) 16(b)	59	Model broke in many pieces at 59 sec	

KT silicon carbide	1	Before and after test; During test	17(a) 17(b)	60	Model remained intact, some oxidation of front face

TABLE 33.—*Description of Models and Tests*

Description of material	Model configuration	Photographs of model	Figure	Duration of test, sec	Reaction of model during test	Remarks
Speer grade 8334 graphite	1	Before test; During test; Repeat test	18(a) 18(b) 18(c)	23 Repeat 26	Graphite oxidized rapidly, model broke into many small pieces.	
Speer grade 3499 graphite	1	Before test; During test; Repeat test with new model.	19(a) 19(b) 19(c)	21 Repeat 21	Glowed extremely bright, model broke into many small pieces.	
Speer grade 8204 graphite	1	Before test; During test	20(a) 20(b)	32	Glowed extremely bright, model broke into many small pieces.	
Great Lakes type R graphite	1	Before test; During test; Repeat test with new model	21(a) 21(b) 21(c)	22.5 Repeat 27	Glowed very bright before breaking into many small pieces	
ATJ graphite	1	Before test; During test; Repeat test	22(a) 22(b) 22(c)	16.5 Repeat 16.5	Glowed very bright before breaking into many small pieces	
Siliconized ATJ graphite prepared by vapor depositing silicon on graphite.	1	Before and after test; During test; Repeat test with new model	23(a) 23(c) 23(b) 23(d)	60 Repeat 60	Very little change, repeat test showed more damage	Silicon oxide appears to increase oxidation resistance of graphite.

TABLE 33 (Continued)—Descriptions of Models and Tests

Description of material	Model configuration	Photographs of model	Figure	Duration of test, sec	Reaction of model during test	Remarks
Silicon carbide bonded graphite	1	Before test--------- After test--------- During test---------	24(a) 24(b) 24(c)	60	Some oxide on front surface.	
ATJ graphite electroplated with chromium	1	Before test---------	25(a) 25(b)	23.5	Model broke up.	
ATJ graphite, electroplated with chromium undercoat, platinum electrodeposited on surface	1	Before and after test- During test---------	26(a) 26(b)	58	Model partially failed.	Better oxidation resistance than graphite.
ATJ graphite, coated with alternate layers of flame-sprayed zirconia and molybdenum, 3 coats molybdenum and 2 layers of zirconia	1	During test---------	27	33	Failure was progressive.	
ATJ graphite, coated with alternate layers of flame-sprayed alumina and molybdenum, 3 layers of molybdenum and 2 layers of alumina	1	Before test--------- During test---------	28(a) 28(b)	32	Failure was progressive..	

denum failed during the test. Of the several grades of graphite tested, siliconized graphite and silicon carbide-bonded-graphite were superior to graphite in oxidation resistance. Refractory materials of silicon carbide, zirconium boride, and siliconized boron successfully withstood the tests.

Rummler (ref. 6), Structures Research Division, NASA Langley Research Center, has carried out basic work in evaluating the performance of molybdenum disilicide coatings on molybdenum. Particular attention has been given to the elucidation of differences in the oxidation process of boron-doped and undoped $MoSi_2$ coatings. Some samples were held at elevated temperatures in still air while others were cyclically heated. The results of this study will be published shortly. Further studies in this program are planned.

Rummler conceived and perfected a new automatic balance with exceptionally long-term stability. This type of balance is very useful for the investigation of coatings, particularly those which are exceptionally oxidation-resistant. Details of the balance will be published in the near future. The balance arm design is shown in figure 104.
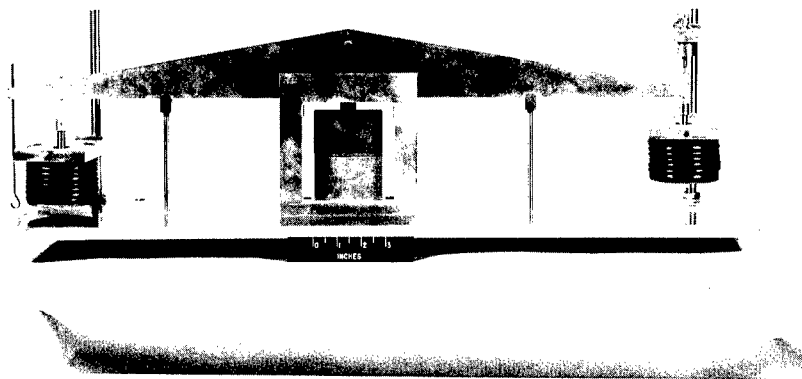
FIGURE 104.—Balance arm and sensor developed for studies of oxidation resistance of coatings for refractory alloys.

COMMERCIAL IMPLICATIONS

NASA contributions have not been large in this area of technology, and the commercial applications for refractory metals must await further developments of coatings. As of this time, too little, firm, cost data are available to estimate the commercial uses of coated refractory alloys. In the absence of reliable cost information, useful life data, and reliability, few commercial applications are likely for coated refractory metals. Potential uses include: high-temperature chemical processing equipment, heat exchangers, and high-temperature heating elements.

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BIBLIOGRAPHY OF INORGANIC COATINGS
AND PIGMENTS

Bibliography of Inorganic Coatings and Pigments

INTRODUCTION

The following bibliography was obtained from a computer literature search directed and conducted by Francis W. Kemmett and Charles Hargrave of the NASA Office of Scientific and Technical Information. The table in this section gives the computer search work sheet used in programming the search. This search was limited to all inorganic coating and pigments abstracts covering NASA and other Government publications indexed and available at the NASA computer search facility in Bethesda, Maryland on December 20, 1963. No documents published before January 1, 1960 were sought because of the authors' desire to encompass only recent information rather than to conduct a comprehensive historical survey. In addition to the computer search, a manual search was made covering non-NASA relevant Government publications not stored in the machine system, but available in the NASA indexes.

An initial editing of the machine and manual search was made to accept those citations which were directly related to inorganic coatings and pigments. Subsequently, the accepted citations were divided into categories which parallel the body of this report. Each division was further subdivided to permit logical access to citations. This bibliography is not presented as a complete subject survey index, but represents a useful listing of NASA and non-NASA Government research and development reports relating to the technology of inorganic coatings.

The reader is also reminded that a review of the references just preceding the bibliography is desirable since time did not permit combining the two. However, the parallel construction of these two indexes makes this task relatively simple for the reader interested in one or several technical areas.

Computer Search Work Sheet

Bibliography No.	4	5	6	7		Problem No.	2	3
	3	5	8	N				

Title of Bibliography: Inorganic Coating and Pigment

Analyst: Neely

Date: Dec. 9, 1963

Item	Term	Term No.	No. of Acc.	Diagram
A	Metal	524864	2266	
B	Intermetallic	425728	51	
C	Ceramic	117632	389	
D	Glass	337984	471	
E	Crystal	173568	1286	
F	Composite	142720	292	
G	Composition	142848	544	
H	Pigment	630272	32	
I	Coating	133888	725	
J	Inorganic	415872	137	
K	Paint	604672	69	
L	Dip	206080	30	
M	Enamel	247424	9	
N	Air	017280	1282	
O				
P	Spraying	792960	82	
Q	Plasma Spraying	639282	1	
R	Flame	283648	454	
S	Vacuum Deposition	917248	21	
T	Vapor Deposition	922624	28	
U	Solution	777536	900	
V	Deposition	194112	198	
W	Electrophoresis	242688	16	
X	Substrate	817024	120	
Y	Thin	859520	507	
Z	Film	280064	814	

Logical Equation

$$L = \underset{1}{(A+B+C+D+E+F+G+J+W+X)} \times \underset{2}{(H+I+K+L+M+V)} + \underset{3}{(N+R+U)} \times \underset{4}{(P)} + \underset{5}{(Y)} \times \underset{6}{(Z)}$$
$$\underset{7}{+ (Q+S+T)}$$

Acceptance Ratio $= \dfrac{\text{No. Accepted Citations}}{\text{No. Total Citations}} \times 100 = \qquad$ Percent

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