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FORMULATION PROCEDURES, RATIONALE, AND PRELIMINARY IMP-H FLIGHT DATA FOR SILICONE PAINTS WITH IMPROVED STABILITY

JOHN B. SCHUTT
CHARLES M. SHAI

DECEMBER 1973

GSFC ———— **GODDARD SPACE FLIGHT CENTER** ————

GREENBELT, MARYLAND

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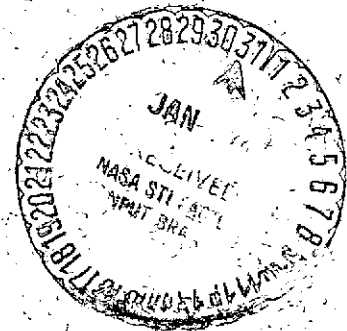
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PREFACE

This report summarizes a five year aerospace paint develop-
ment effort by cognizant personnel of the Thermophysics Branch,
Coatings Section, under the Engineering Physics Division at
GSFC. The results of some of the more significant experiments
are made use of in the second section of this report, which is
concerned with unifying deductions from these data into a single
representation of the paint stability problem. Hopefully, this
phase is carried out with sufficient brevity and clarity to demon-
strate that chemical behavioral explanations can be provided in
terms of known inorganic species. The chemical stabilities of
zinc oxide and titanium dioxide are treated in parallel fashion,
and evidence footnoted which indicates that titanium dioxide is
responsible for the accelerated disintegration of exterior paint
systems used on terrestrial applications.

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ABSTRACT

This report details a class of silicone paints undergoing space qualification on IMP-H. In addition to ultraviolet irradiation, samples are presently reclining about 10^{16} solar wind protons per year. Preliminary data, covering the time span of the first anniversary, give incremental solar absorptances of 0.03 for two white paints, and 0.01 for leafing aluminum and a green tinted white paint. Complementing these data are complete descriptions of techniques used in making these paints, stabilizing the zinc oxide pigment, and choosing a solvent. Outgassing characteristics of finished coatings are also included. An attempt toward unification of these various aspects of the aerospace paint problem is provided through documented photochemical reactions, and a generalized band representation of the problem and its solutions.

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INTRODUCTION

During the later part of the nineteen fifties, it was discovered that zinc oxide powder in combination with a silica buffered potassium hydroxide solution yields an ultraviolet stable thermal control coating, suitable for spacecraft.[1] Efforts centered around modifications to this basic coatings system have continued to be fruitful because ultraviolet stability aimed at minimum solar absorptance remains the dominant requirement for stable thermal control. So long as gradual damaging due to protons at temperatures of 25°C or less can be tolerated, zinc oxide and mixed pigment systems processed with zinc oxide will be acceptable, and, will provide the only solution to the stability problem. Modifications of this coating system have centered around increasing the compatibility between pigment and silicone resin system. The silicone system is desirable because it provides improved mechanical properties together with simpler and less critical application procedures.

One of the more interesting aspects of this work to date, as conducted elsewhere, has been the application of solid state concepts to gain a general picture of the stability problem appropriate to paint systems. Strangely enough no activity has been directed toward understanding the zinc oxide-potassium silicate stabilization synergism, but rather energies have been directed toward gaining an understanding of titanium dioxide photochemistry,[2] the photochemistry of zinc oxide in single crystal form in aqueous media containing recombination centers such as iron, cobalt, manganese, to name a few,[3] and the relationships between oxygen degassing and the photochemical behavior of zinc oxide powders.[4]

Omission of studies of the zinc oxide-silicate synergism can perhaps be rationalized by alluding to the fact that characterization of alkali-metal silicate solutions is difficult, and at the concentrations of ingredients used in paint preparation electrochemical laboratory techniques and theories are difficult to apply.

Because zinc oxide and potassium silicate behave well toward ultraviolet light, it was assumed that zinc oxide was intrinsically stable, and should, as a consequence, perform well in a silicone binder. Such turned out not to be the case. McKellar et al.[5] demonstrated that zinc oxide was intrinsically unstable by checking its post irradiation reflectance in-situ. Prior to this work the dimethyl silicone based system appeared stable only because measurements were carried out in air; it is now well established that the time elapsed between

breaking vacuum and making an air measurement is more than sufficient for reabsorption of the required surface oxygen species and annihilation of free electron absorption. Logically then, the subsequent approach was to replace the zinc oxide with the demonstrated uv resistant dehydrated zinc oxide-potassium silicate system as a filler in the dimethyl silicone binder (S-13-G).[6] This was successfully accomplished after carrying the corticated powder through an elaborate elutriation scheme to 1) promote the shelf-life of the paint, and 2) minimize unwanted degradation at the corticator-binder interface.

Broadly speaking, the efficacy of the buffered alkali-metal silicate solutions, as a class, evolves somehow from the solubility of zinc oxide powder in alkali, and therefore its ability to significantly alter the surfaces of these particles. In solid state jargon, we can state quite generally that the interaction depresses the band edges by changing their curvatures at the surfaces of the particles, and, as a result, increasing the conductivity of the surface layer.

An alternative treatment, proposed by Morrison, has already been alluded to, namely, the single species concept capable of providing equilibrium between two valence states chosen because their cross sections are suitable for electron and hole capture. The Morrison system, operating at a lower pH level, 8.5 instead of 11 to 13 in the silicate-system, can have little effect on band curvature. It operates by placing a center for electron capture just below the conduction band of zinc oxide, and a center for hole capture between the valence and Fermi level.

Pertinent aspects of our work, are given below in summary form as a series of photochemical reaction schemes deduced from wet chemical experiments. These relate to the nature of titanium dioxide, and are presented giving due consideration to the behavior of zinc oxide under similar circumstances.

These aspects are then reinterpretated using band scheme nomenclature in an effort to relate them to Morrison's work.

Descriptions are given for making, formulating, and applying silicate buffered zinc oxide paint system utilizing an oligomer of methyl silanol oligomer as binder (OI-650B).* As is documented below, the paint system has good combined ultraviolet-proton stability as determined from the IMP-H Thermal Control Monitoring Experiment.

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*Reference to a version of this material as supplied by Owens Illinois Corporation.

SOME CHEMICAL AND PHYSICAL ASPECTS
OF THE STABILIZATION PROBLEM

In presenting the stabilization problem and approaches to its solution, both zinc oxide and titanium dioxide will be discussed. This approach is taken because both pigments are universally used in paint technology, both are n type semiconductors, and both have band gap energies in the neighborhood of 3 ev. The similarity ends there however. From the point of view of aerospace technology, zinc oxide was initially judged ultraviolet resistant because 1) optical measurements were carried out initially in air before an in-situ apparatus was first designed and built and 2) a silica buffered potassium hydroxide solution was used to formulate it into a coating. The potassium silicate slurry of zinc oxide, it turned out, served to inhibit photoxidation. Acidic treatments, on the other hand, accelerated photolysis. Quantitatively, this behavior is in keeping with simple zinc oxide chemistry,

$$ZnO + 2 \ ^-OH \xrightarrow{\text{H}_2\text{O}} ZnO_2^= + H_2O,$$
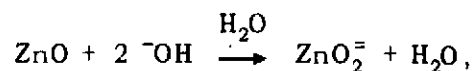
where the zinc ion is not stripped of its oxygen ligand, and the oxygen for water formation is supplied by the base. On the other hand

$$ZnO + 2 H^+ \xrightarrow{\text{H}_2\text{O}} Zn^{++} + H_2O,$$
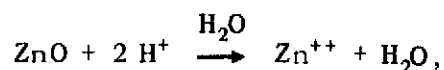
where the oxygen to form water is supplied by the zinc 'oxide lattice', and stripped free by protons (holes). In the former case, we can think of populating the surface with $M^+ \ ^-OH$ rather than $H^+ \ ^-OH$ as in the usual hydroxylation reaction. Normally hydroxylation is pictured
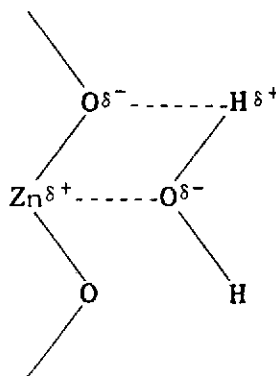
where populating occurs through a hydrogen bonding intermediate. Analogously, we simply replace a proton (H^+) with say potassium (K^+) and write

$$
\begin{array}{c}
\diagdown \\
O^{\delta^-} ------ K^{\delta^+} \\
\diagup \quad\quad\quad \diagup \\
Zn^{\delta^+} ----- O^{\delta^-} \\
\diagdown \quad\quad\quad \diagdown \\
O \quad\quad\quad H \\
\diagup \\
\end{array}
$$
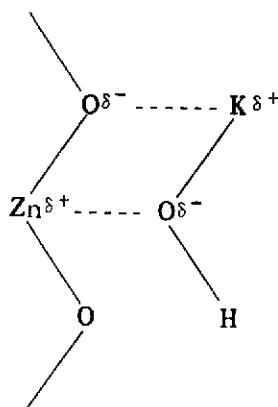
to give $K^+ \ ZnO_2^-$ in solution. The stabilizing effect of alkali silicate corticants must, therefore, possess a photochemical analog to this behavior in controlling surface reactivity.
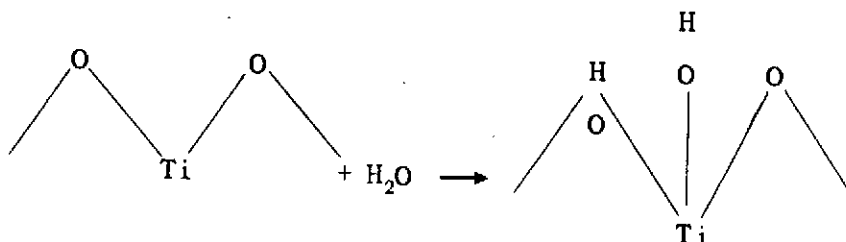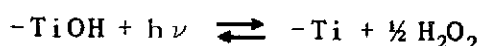
Focusing attention now to titanium dioxide, we recall that its chemistry is more subtle because simple and base reactions cannot be written down: this aspect holds true for both anatase and rutile types.

In studying titanium dioxide in our laboratory, most attention has been paid to anatase because it is an ideal host for impurities by virtue of its open crystalline network. Stuffing the interstices with an alkali metal ion either alone or in conjunction with a heavy metal can give rise to a phenomenon we termed thermophototropism.[7,8,9,10] This characterization, thermophototropism was applied, because optical recovery was induced by heating, and not by removal from the ultraviolet source. The occurrence of the phenomenon, in most cases, requires the presence of an inorganic base — alkaline earth hydroxides also work — for activation, but acidic treatments are ineffective. In parallel with zinc oxide, titanium dioxide responds differently toward acids and bases as is exemplified by its reactivity in the presence of ultraviolet light, moisture, and, for example, benzene. From these experiments a less obvious chemical behavior can be written down based on the ability of titanium dioxide to dissociate water, namely,

$$
\begin{array}{c}
O \qquad\qquad O \\
\diagup \diagdown \diagup \diagdown \\
\diagup\quad\diagdown\diagup\quad\diagdown \\
Ti \qquad + H_2O \longrightarrow
\end{array}
\qquad
\begin{array}{c}
\qquad\qquad H \\
H \quad O \quad O \\
\diagup \diagdown \mid \diagup \diagdown \\
O \quad\mid \\
\diagup\quad\diagdown\mid\diagup\quad\diagdown \\
Ti
\end{array}
$$

where two types of hydroxyl moieties occur, since the titanium ions will in general be depressed beneath the oxygen layer to permit screening of positive charges. During irradiation, a photon of about 3 to 4 ev may excite either an oxygen based electron comprising the hydroxyl populations as well as a lattice oxygen. Of the possible excitations, one must involve a charge transfer process, ultimately reducing a titanium ion while oxydizing a surface hydroxyl oxygen.
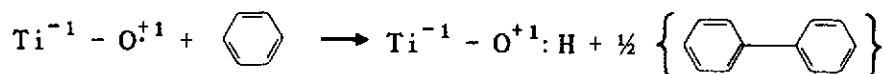
For the case of pure anatase or rutile powder, there results the formation of hydrogen peroxide, viz.,

$$-TiOH + h\nu \rightleftharpoons -Ti + \tfrac{1}{2} H_2O_2$$

such that in benzene

$$Ti - O + h\nu \rightleftharpoons Ti^{-1} - O^{+1}_{\cdot}$$

followed by[11]

$$Ti^{-1} - O^{+1}_{\cdot} + \bigcirc \longrightarrow Ti^{-1} - O^{+1}:H + \tfrac{1}{2} \left\{ \bigcirc\!\!-\!\!\bigcirc \right\}$$

where the oxygen radical extracts a hydrogen atom from benzene thereby stabilizing the transferred charge. The extraction reaction must occur during the lifetime of the charge transfer excitation. Since it has also been established that anatase will reduce ferric ions to the ferrous state in acid solution in the presence of about 3-4 ev photons,[12] the photochemistry can be diagrammed for iron doped anatase activated at 800°C during the iron catalyzed transformation to rutile,[13] viz.,

Chromophoric intermediate
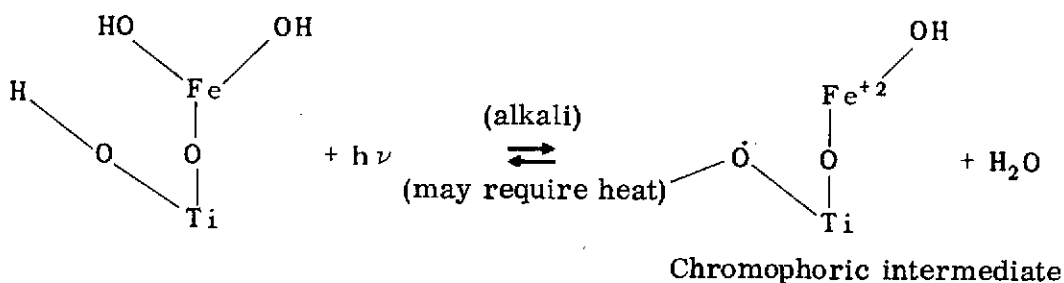
for the case where the iron oxide nucleus attaches itself to a hydroxylated
titanium site, and

$$HO-Fe^{+3}(-OH)(-O-Ti)(-O-H \cdots Ti) + h\nu \rightleftharpoons HO-Fe^{+2}(-OH)(-O-Ti)(-Ti) + H^+ + \tfrac{1}{2}O_2,$$

remembering

$$H_2O_2 + h\nu \longrightarrow \tfrac{1}{2}O_2 + H_2O,$$
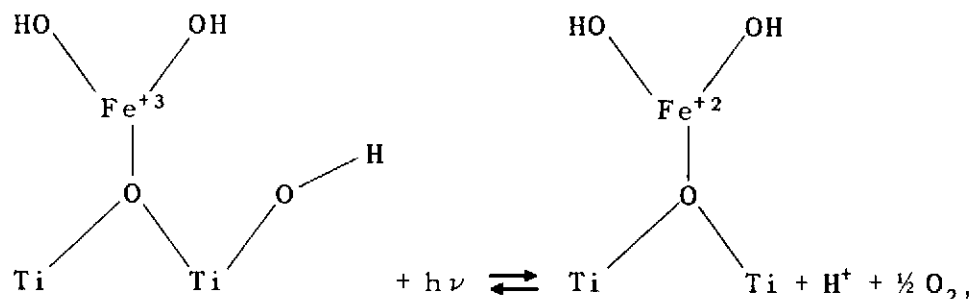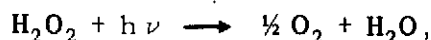
where the iron oxide has become attached to a lattice oxygen. The latter case
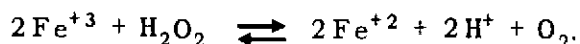is the solid state analog of the reaction:[14]

$$2Fe^{+3} + H_2O_2 \rightleftharpoons 2Fe^{+2} + 2H^+ + O_2.$$

In both cases stabilization depends upon the presence of water in some form
prior to excitation of -OH by the incident photon. The latter case shows the iron
hydroxylated, but this need not be the case; a priori, $-Fe = O \cdot H_2O$ may be just
as good representation. Conclusions are the same for each instance, only reac-
tion rates will change.

To summarize the behavior of "pure" titanium dioxide use must be made of the
fact that it is an n-type semiconductor, which like zinc oxide implies that a re-
duced "impurity" like O_2^- [15] can populate the surface along with hydroxyls.
Starting with

$$Ti(-OH)(-OH) + h\nu \rightleftharpoons Ti(-OH) + \cdot OH$$
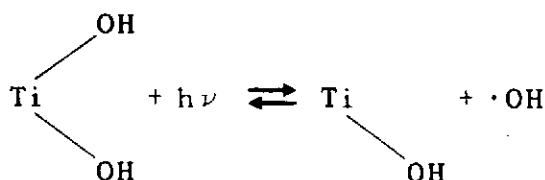
a deoxygenation reaction can be postulated, e.g.,

$$Ti \diagdown_{OH} + \cdot OH \rightleftarrows Ti \diagup_{O} + H_2O$$
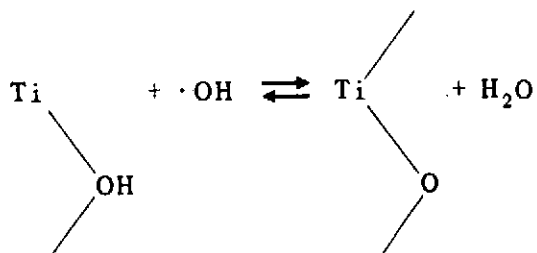
or a dehydration in the manner of

$$Ti \diagdown_{OH} + OH \rightleftarrows Ti \diagdown_{O} + H_2O.$$
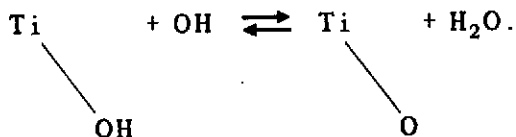
Since titanium dioxide will only lose oxygen under fairly drastic conditions, dehydration would be favored in the absence of O_2^-. In the absence of O_2^- then many reactions are documented and the formation of H_2O_2 follows in simple fashion:[16]

$$Ti \underset{OH}{\overset{O}{—O—H}} + O_2 + h\nu \rightleftarrows Ti \underset{OH}{\overset{O}{—O}} + H^+ \quad ^-O_2$$

$$O_2^- \mid H^+ \longrightarrow HO_2$$

$$\text{Ti}\diagdown\!\text{OH} + \text{HO}_2 \rightleftharpoons \text{Ti}\diagdown\!\text{O} + \text{H}_2\text{O}_2$$

$$\text{O}\diagup\text{Ti}\diagdown\text{OH} - \text{OH} + h\nu \longrightarrow \text{O}\diagup\text{Ti}\diagdown\text{OH} + \cdot\text{OH}$$

$$^-\text{O}_2 + \cdot\text{OH} \longrightarrow \tfrac{1}{2}\,\text{O}_2 + \text{HO}_2^-$$

$$\text{Ti}\diagdown\!\text{OH} + \text{HO}_2^- \longrightarrow \text{H}_2\text{O}_2 + \text{Ti}\diagdown\!\text{O}$$

$$^-\text{O}_2 + \cdot\text{OH} \longrightarrow \,^-\text{O} + \text{HO}_2$$

$$^-\text{O} + \text{H}_2\text{O} \longrightarrow -\text{OH} + \,^-\text{OH}$$

$$\text{Ti} + \,^-\text{OH} \longrightarrow \text{Ti OH}$$
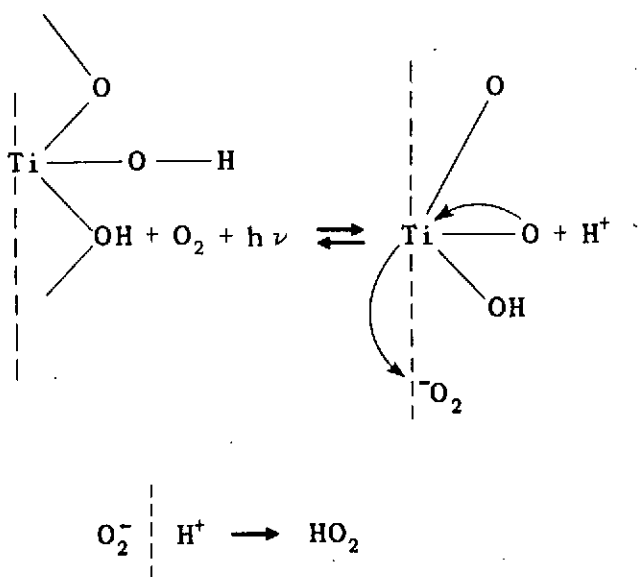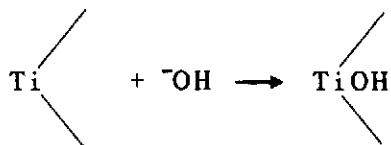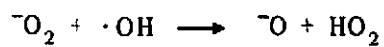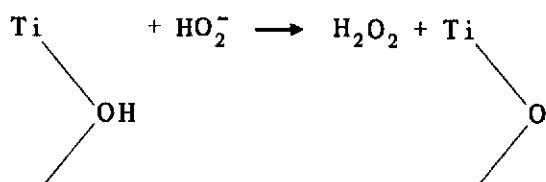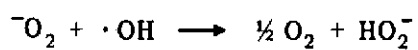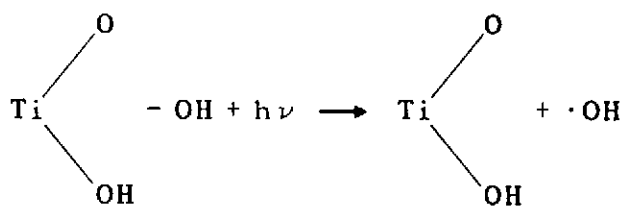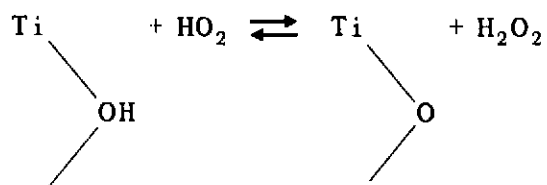
In other words titanium dioxide oxidizes water giving oxygen in the presence of transition metal impurities and water, and/or in the presence of oxygen and water

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in the presence of ultraviolet light.* Some simple evidence why zinc oxide cannot do this without losing lattice oxygen has already been given. This property of zinc oxide has been treated in depth by Morrison and Freund.[17] Another difference in reactivity between these electrically and optically similar oxides will now be cited. Zinc oxide reacts with carbon dioxide whereas titanium dioxide does not. Carbon dioxide has the options of combining with a lattice oxygen or dissociating chemisorbed oxygen, viz.,

$$4\,O_2^- + 2\,CO_2 \longrightarrow 2\,CO_3^= + 3\,O_2,$$
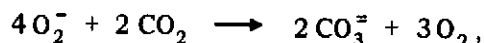
where the requirement of a paramagnetic species is met as in the reaction with chromic oxide doped zinc oxide.[18] At pH > 8.5, the sequence[19]

$$2\,{}^-OH \longrightarrow H_2O + O^= \;\; (\text{lattice})$$
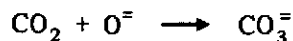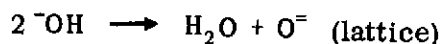
$$CO_2 + O^= \longrightarrow CO_3^=$$

could occur at a solid-gas interface. We are now in a position to put together the above information in a manner suggestive of how alkali, and more particularly, alkali metal silicate solutions serve so effectively to stabilize zinc oxide powder.

The primary photon absorption process is

$$ZnO + h\nu \longrightarrow h + e$$

after which

$$h + O^= \rightleftarrows O^-$$

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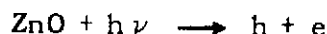
*The ability of TiO_2 to react according to the photochemical processes just discussed in the presence of water makes it partially responsible for the rapid disintegration of exterior paints for wood and metals.

and

$$h + O_2^- \longrightarrow O_2$$
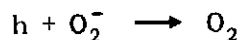
must be prevented if possible. In the presence of alkali media

$$O_2^- + M^+ \longrightarrow O_2^- M^+$$
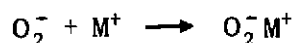
serves as an O_2^- immobilizing reaction by repelling holes and preventing

$$O_2^- + H^+ \longrightarrow HO_2$$
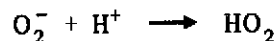
from occurring. Hydroxyl ions would be expected to perform the limited function of complexing with holes,
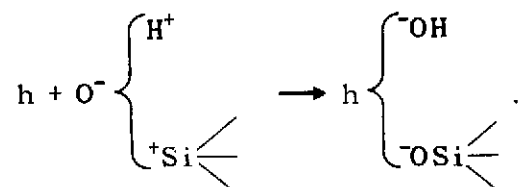
In the presence of heat and light

$$2\ ^-OH \longrightarrow O^= + H_2O$$

can occur and function to inhibit the fundamental photolysis reactions. Because the decomposition products are gaseous, a diffusion barrier against their escape is necessary. On the face of it, this reasoning may appear artificial, but before a lattice oxygen escapes many electronic and lattice effects must cooperate to free the atom; the barrier retards material losses and has the net effect of decreasing the overall reaction rate. The barrier effectiveness is further realized, especially in the case of an alkali silicate matrix, because of the solubility of zinc oxide in alkali. These results are summarized in Figure 1.

10
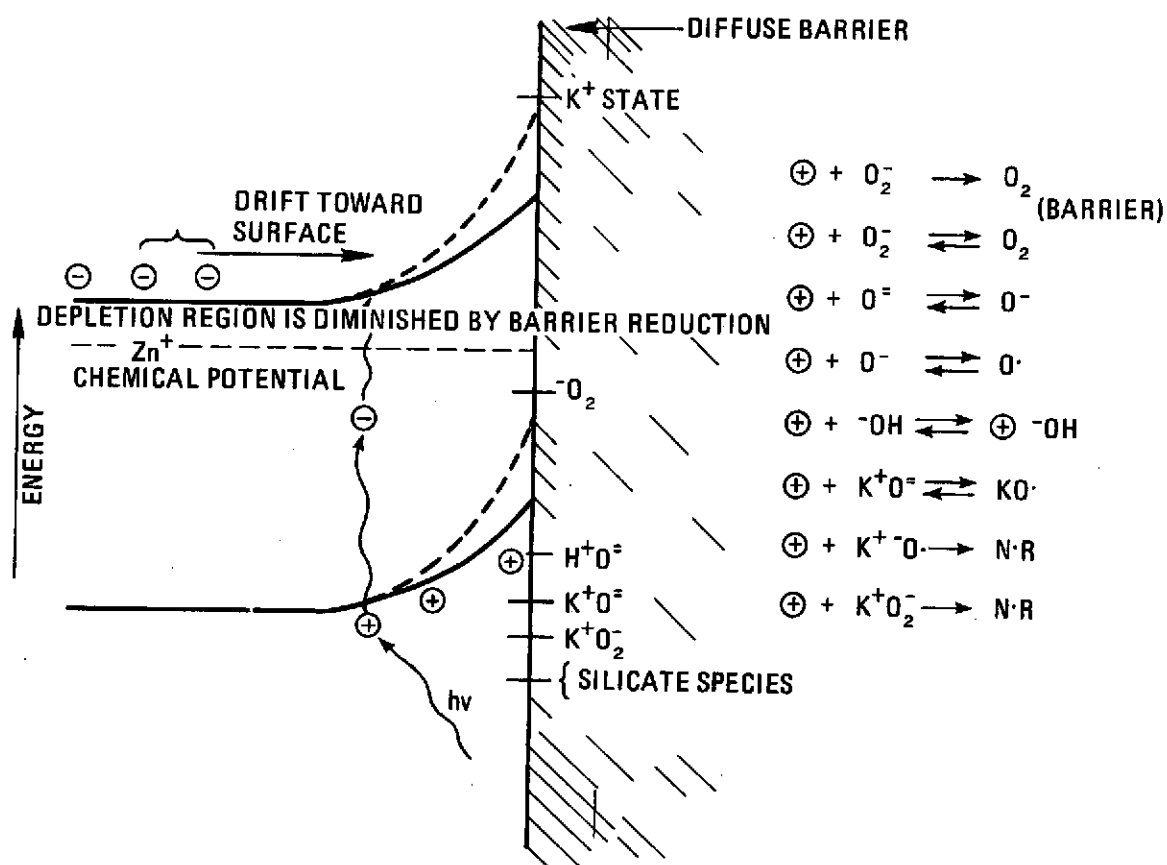
Figure 1. Band Representation of Alkali-Metal Silicate Stabilization Mechanism

At a lower surface pH, the Morrison surface treatment is effective for the powder per se, but can only be retained on the pigment surface with difficulty during paint the formulating process. This system relies on a steady state electron transfer in the presence of photons between recombination centers having capture cross-sections optimized with respect to zinc oxide. Iron ions meet this criterion, and form a recombination center because

$$\mathrm{Fe_A^{+3} + Fe_B^{+2} \rightleftharpoons Fe_B^{+3} + Fe_A^{+2}}$$
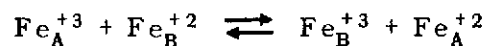
occurs with activation energy O (k T). The system is a dynamic one in carrying out the stabilization function whereas the alkali metal silicate functions primarily by shifting surface states by virtue of its chemical reactivity out of the range energy-wise where oxidation by holes is probable: the alkali-metal silicate is not as good a conductor as the ferrous-ferric couple, but increases the conductivity of the zinc oxide surface (decreases band curvature). The Morrison and alkali-silicate treatments therefore function similarly from the viewpoint of pigment stabilization, but differ significantly with respect to ease of implementation.
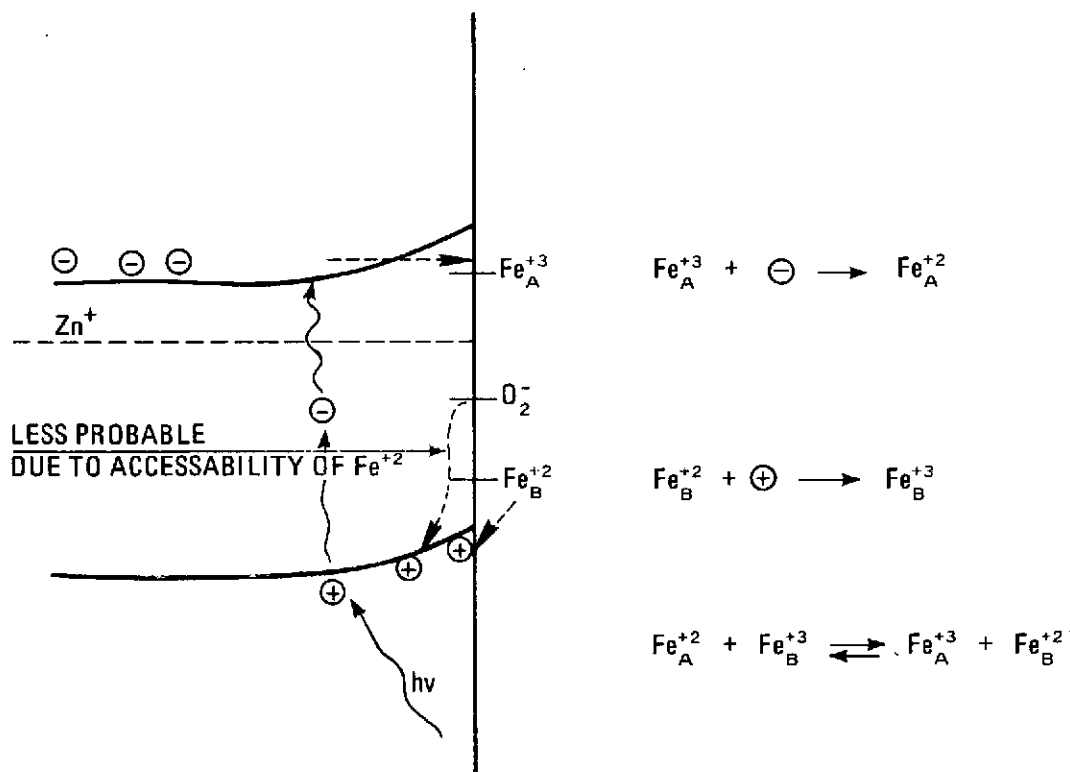
Figure 2. Band Representation of Morrison Stabilization Mechanism

FORMULATING PROCEDURES

Pigment Preparation

In treating zinc oxide with silica buffered alkali metal hydroxides for purposes of environmental stabilization, it is critical that the weight relationship of alkali metal silicate solids to zinc oxide be such that the pH of the resultant slurry be in the critical range of 11-13. If the slurry drops below pH 10, a condition that can possibly be induced by excessive ZnO, which itself buffers in the range of pH 8.3-8.5, then silica can react preferentially with itself instead of reacting with the surface layers of the pigment. It is the reactivity of the buffered alkali silicate with zinc oxide in solution which enables consecutive reactions with silica to take place during the dehydration procedure, thereby establishing a diffuse graduated silicate interface between pigment layers. The rationale for thus modifying the ZnO is:

1) To improve ultraviolet stability by removing states from the gap,

2) To provide a partial barrier to low energy proton penetration.

To accomplish the treatment in an optimized manner, the pigment must be added to the treatment solution while the combination is under agitation, until the resulting slurry is finely dispersed. Once dispersed the mixture is stored in a noncontaminating container such as polypropylene for a minimum reaction time period of about one week. An upper limit on time need not be set. As reactions proceed, the mixture assumes a ropey behavior when poured prior to dehydration. Table 1 below shows compositions for treatment solutions.

Table 1

Concentrations and Ranges of Silicate Buffering Solutions for ZnO

Wt. % Silicate Solids*	Int. ZnO	Wt. Silicate Solids	pH	Water Total	Mole Ratio* (SiO_2/M_2O)
7%	300	21	11-13	271	2.1-4.8
12.7%	300	38	11-13	440	2.1-4.8

*See Appendix II for a brief description of the characterizations of silicate solutions.

The water level is quite flexible, but does control the rate of reactivity and degree to which the chemistry proceeds to completion. Excessive water slows the reaction. For surface treating the ZnO, silicates of sodium, potassium or lithium may be used. Care must be employed, however, in formulating with lithium silicate because lithium ions are small enough to diffuse into the zinc oxide particles to such an extent that particle disintegration may result. In general then lithium silicates would be used in conjunction with potassium or sodium silicates, the environment of which causes lithium silicate or mixed lithium-potassium or -sodium crystals to form. It is the ability of lithium silicates to dehydrate in the presence of potassium or sodium silicate buffers which makes their use attractive. The ability of lithium silicates to dehydrate more easily than their counterparts means that they will tend to accumulate at surfaces making for less porous cortications, thereby inhibiting the outward diffusion of potassium and sodium ions.

After storage for at least one week the zinc oxide slurry is ready for dehydration. The removal of water may be taken care of by heating in a circulating air oven at 110°C with occasional stirring, or in a microwave oven, turning the material at 1 minute intervals. Dehydration by microwaves is considerably faster, while at the same time cleaner because contamination is less of a problem. Processing a quart of slurry in this mode requires about 40 minutes carried out in two batches.

After being dehydrated by microwaves the material is friable, and is readily ground in a ball mill. In milling, the crucial aspects are to grind in the proper liquid medium, and for the proper length of time. The preferred medium is 200 proof, 100 percent CP ethyl alcohol because dehydration continues during the milling process, which must not exceed 20 minutes. Following milling, the ethyl alcohol is evaporated over the range of 80-120°C, and the powder stored in fresh alcohol. In lieu of alcohol storage, the pigment may be stored in a desiccator under vacuum or dry nitrogen.

Processing the heated pigment in this manner increases compatibility with the binder, improves shelf life of the paint, and promotes coating integrity by eliminating almost all of the chemisorbed water from the treated pigment — a barrier to polymerization.

Paint Formulation

For small batches, up to a quart or so, the coating is most easily prepared by blender. The required materials are listed in Tables 2, 3, and 4 below. Preparing formulation 1 in Table 2 is initiated by dissolving the methyl silanol oligomer in dioxane; a preliminary stock solution on a one to one basis, dioxane

Table 2

Compositions in Parts by Weight for White Paint

	Range Table by Weight		
	1	2	3
Ingredient	Parts by Wt.	Parts by Wt.	Parts by Wt.
Methyl Silanol Oligomer	10	10	10
Solvent (Dioxane)	50	44	63
Pigment, Corticated ZnO	40	35	50
Total	100	89	123

Table 3

Compositions in Percentages for White Paint

White Composition	Range Table by Percentages		
	1	2	3
Ingredient	Parts by Wt.	Parts, %	Parts, %
Methyl Silanol Oligomer	10	11.2	8.1
Solvent (Dioxane)	50	49.4	51.2
Pigment, Corticated ZnO	40	39.4	40.7
Total (%)	100.0	100.0	100.0

Table 4

Pigment Ranges for Green Paint by Approximate Solar Absorptance

Ingredient	Weights			
Corticated ZnO	40	40	40	0
Cr_2O_3	0	0.5	1	40
Solar Absorptance of Resulting Paint	.18-.20	0.36-0.38	.40-.45	0.63-0.68

Amounts of resin solvent vehicle are indicated in Table 2.

to resin, may be made up, first, or the entire required amount of dioxane may be used. This latter solution will then be 17 percent total resin solids. Continuing formulation, the pigment is now added slowly to the blending resin solution until the ratio of pigment to resin is 4:1. Care must be taken to assure that the mixture remains cool, otherwise polymerization gelation may begin prematurely, or the pigment-resin system might commence to react.

The paint must in general be made up prior to use because the shelf-life is only a few hours, but since solution of the resin in dioxane occurs in minutes, and the pigment blending can be achieved in fifteen or so minutes, the system can be used as a two part system without difficulty.

Application of the coating is achieved by standard spray technique until 3-5 mls are applied. Prior to application the substrate must be made grease and dirt free. Abrading is not essential. Curing is carried out first at 70-80°C for several hours prior to raising the temperature to 120°C-150°C for 18 hours. The latter temperature rids the coating of dioxane, unreacted resin, and completes the polymerization.
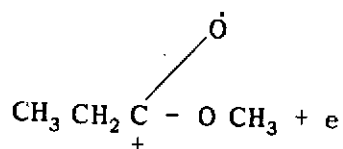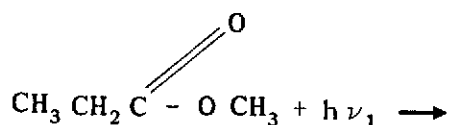
Elimination of unreacted oligomer and dioxane from the paint serves two purposes: first, to increase environmental stability and second, to significantly reduce the tendency for spacecraft self-contamination.
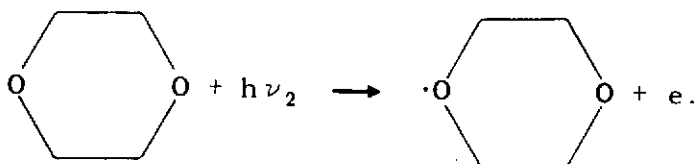
CHOOSING A SOLVENT SYSTEM

A solvent system serves to give to a pigment-binder composition many desirable properties necessary to handling, and application. In addition, a proper solvent

system assures post application properties such as proper cure, a cosmetic appearance, and the desired degree of specularity. However, whenever stability toward outer space environments is of utmost importance, solvent selection must also be considered for its resistance to photoylsis and chemical reactivity in the presence of pigment corticants (surface stabilizing layer(s)) during formulation and cure. From the point of view of photolysis, esters, particularly ethyl acetate[18] are the preferred solvents for the methyl silanol oligomer.

As a basis for comparison with dioxane we write

$$CH_3 \, CH_2 \, C \overset{\displaystyle \nearrow O}{} - \, O \, CH_3 + h \nu_1 \longrightarrow$$

$$CH_3 \, CH_2 \, \underset{+}{C} \overset{\displaystyle \nearrow \dot{O}}{} - \, O \, CH_3 + e$$

and

the stability criterion requires therefore that $\nu_1 > \nu_2$ for the generation of an electron-hole pair. Once generated, the lifetime of this combination is determined by the dielectric properties of the surrounding matrix and resonance energy of the oxidized solvent molecule.

If we assume now that the pigment-binder-solvent system can be heated to release virtually all solvent, another aspect of solvent choice becomes relevant, and that is the lowering of system free energy gained from corticant-solvent reactivity.

Zinc oxide, when slurred in water, reacts to give a pH of 8.3 to 8.5. Since it is an n type semiconductor, this pH information requires that photolytic stabilization can only be accomplished at pH's $\geq$ 8.3 to 8.5. To relate this observation

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to the two solvents under discussion, we can write

$$CH_3\ CH_2\ \overset{\displaystyle O}{\overset{\|}{C}} - O\ CH_3\ +\ MOH\quad \underset{}{\overset{TRACE\ H_2O}{\rightleftharpoons}}$$

$$CH_3\ CH_2\ \overset{\displaystyle O}{\overset{\|}{C}} - O\ M\ +\ CH_3OH$$

and

$$O \bigcirc O\ +\ MOH\quad \overset{TRACE\ H_2O}{\longrightarrow}\quad N.R.\ ,$$
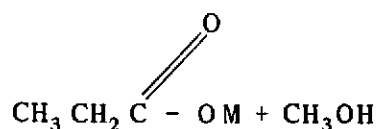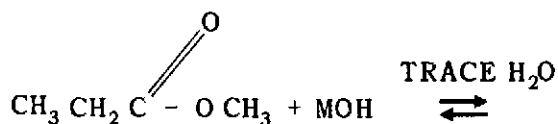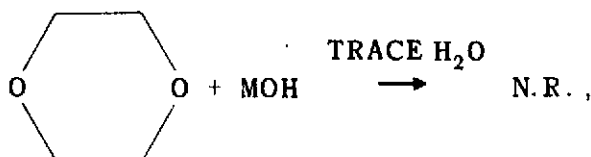
therefore, although dioxane is easier to photolyze, it is inert toward high pH levels, whereas ethyl acetate is not. Trace amounts of acetate salts cannot be readily removed by heating, whereas dioxane although considered a high boiling solvent, can be removed. From an applications point of view it also extends the wet edge, thereby aiding film formation.

ENVIRONMENTAL STABILITY

IMP-H was launched on 22 September, 1972 into a nearly spherical orbit with perigee 32 Re, apogee 39 Re, and inclined 29° to the ecliptic. It is easy to assess from these orbital parameters that the spacecraft does not intercept trapped particles, but rather only those particles comprising the solar wind spectra. From the quiescent solar proton density, $8.4 \pm 4.6\ cm^{-3}$, and speed, 3×10^2 km/sec,[21] the yearly dose, O, is readily found to be in the range

$$3.9 \times 10^{15} < O < 1.3 \times 10^{16}\ protons/cm^2\ yr$$

Since IMP-H was launched during a period of reduced sunspot activity, energetic particles, that is protons with energies greater than 10 Mev, will not significantly

surpass a yearly dose of 10^7 over the energy range of 10-30 Mev. The next solar active period will commence gradually in 1975, and build up until 1977, after which time the average yearly dose will maintain itself in the neighborhood of 10^{10} over the energy range of 10 to 60 Mev, and sustain itself until completion of the 21st seven year cycle.[22] This level serves as a lower bound because increased fluxes arising from eruptions of short duration are not included. IMP-H environmental effects data for two different cortications of zinc oxide are shown in Figure 3. Figure 4 gives the effects of the same environment on the leafing aluminum paint and a chrome oxide tinted version at the silicone system with one of the corticated zinc oxide pigments. From Figure 3, it is clear that the choice of pigments may not be critical.

OUTGASSING CHARACTERISTICS

The degree of polymerization of the methyl silanol binder, and the preferred solvent used in formulating these paints prohibits them from meeting the current outgassing requirements for spacecraft materials: 1% weight loss and 0.1% VCM. Therefore, to meet this specification these paints must be heated to at least 120°C, and preferably as high as 150°C, for purposes of tying in the oligomer, and getting rid of the high boiling dioxane solvent. Comparative outgassing data for these paints is listed below in Table 5.

Table 5

Compilation of Available Outgassing Data Obtained from Reference 22

Paint by Corticant	Cure T°C		Wt. Loss %	VCM %
Sodium–Silicate treated ZnO	(1)	95 – 18 hr	1.786	0.568
	(2)	150 – 18 hr	0.677	0.220
Lithium–Potassium Silicate treated ZnO	(1)	95 – 18 hr	1.409	0.586
	(2)	150 – 18 hr	0.584	0.064
Chrome Oxide Lithium-Potassium Silicate treated ZnO	(1)	50 – 18 hr	2.755	0.950
	(2)	95 – 18 hr	1.043	0.471
	(3)	150 – 18 hr	0.119	0.004

Note: Formulation was a 4:1 solids/resin ratio. Heating performed at atmospheric pressure.
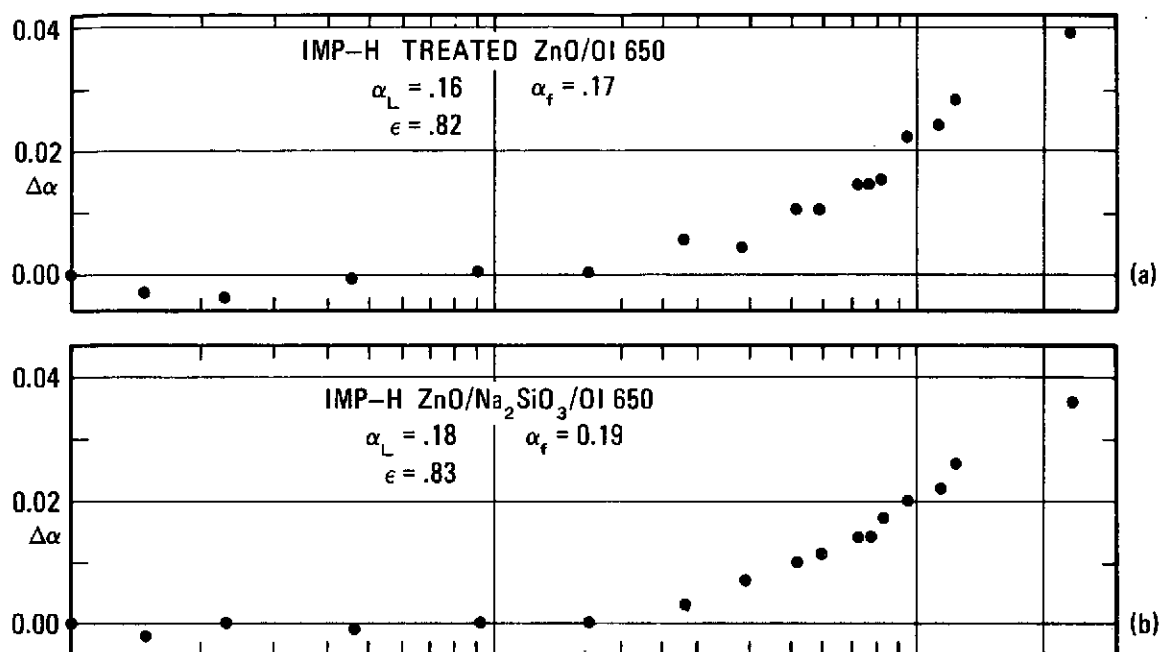
Figure 3. IMP-H Data for a) Lithium-Potassium Silicate Corticated ZnO,
b) Facsimile of (a) Employing Sodium Silicate. α_L and α_F Refer
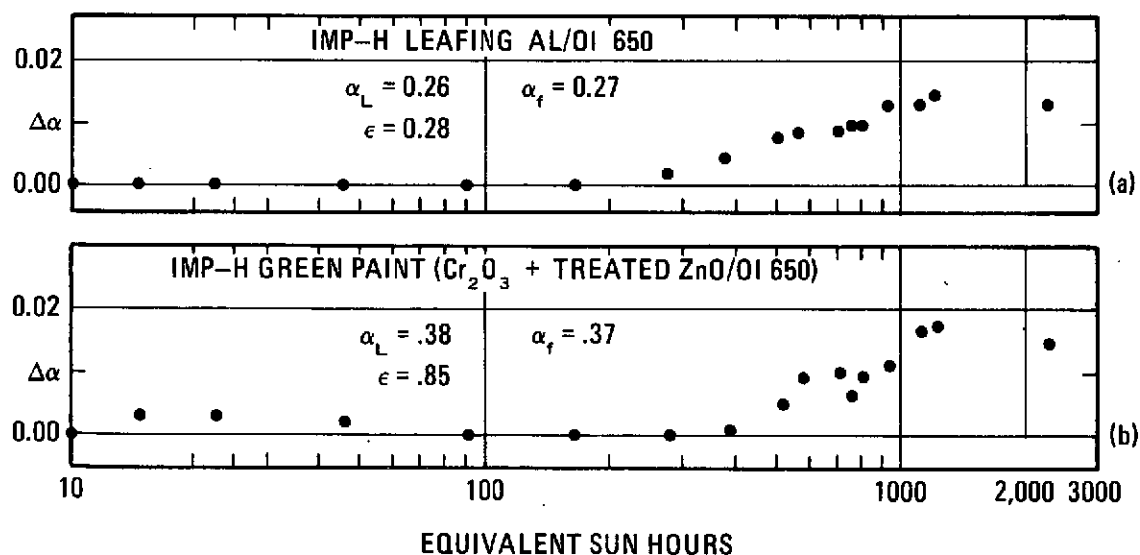to Solar Absorptances Obtained from Laboratory and
Flight Measurements, Respectively.

Figure 4. IMP-H Data for a) Leafing Al Version of OI-650 Paint, b) Corticated
ZnO OI-650 Paint with Chrome Green Tint

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APPENDIX I

GENERAL PROCEDURE

Preparation and Procedures for OI-650 Silicone Oligomer Based Paints
Made from Corticated Zinc Oxide

I. Equipment and Raw Materials

    (A) Heavy duty blender, preferably Oster type.

    (B) Zinc oxide, New Jersey Zinc SP-500 type factory calcined.

    (C) Silicone Oligomer, manufactured by Owens Illinois, type OI-650 stage B (flake form).

    (D) Potassium Silicate Solution; PS-7 by Sylvania Electronic Products (Towanda, Pa.), or, Kasil 6 or 88 by Philadelphia Quartz.

    (E) Sodium Silicate by Philadelphia Quartz, sold as Star Grade.

    (F) Lithium Silicate Solution, instructions are given below for making a version of this solution.

    (G) Chromium Oxide Green, Fisher Scientific

    (H) Leafing Aluminum; MD-5100, manufactured by Metals Disintegrating Co.

    (I) Carbon Black, Channel Black 999 or Conductex for a conductive paint. Both types are manufactured by Columbian Carbon. Conductex is obtainable from Cabot, XC-72R.

    (J) Dioxane solvent, Fisher Scientific

        NOTE:[24] Use with sufficient ventilation to prevent inhalation. Do not allow contact with oxidizing agents.

    (K) Distilled Water

II. Dissolving OT-650 Silicone Resin

(A) Place equal parts by weight of OI-650 B and dioxane into a glass container and occasionally swirl. Mechanical mixing is not necessary; solution occurs rapidly if the resin is in prepolymer flake form. If, however, the formation of a crystal clear solution without turbidity is not possible, the resin has autopolymerized and is not suitable for paint making. It should be discarded. Store prepolymer resin in a refrigerator. Mix with solvent prior to use, do not store the solution.

III. Treatment of ZnO with Sodium Silicate

Ingredients	Parts by Weight
(A) Zinc Oxide, SP-500 Calcined	100
(B) Star Grade Sodium Silicate, liquid form	33.3
(C) Water	50

(D) First add the sodium silicate solution to a glass blender jar, then add the water. Allow mixture to equilibrate. Slowly add the ZnO, while blending until a smooth mixture is obtained. Store in unplasticized polyethylene or polypropylene containers. Shelf-life is indefinite; resistance to proton damage improves with aging; resistance to uv is assured once the pigment is completely wetted by the treatment solution.

IV. Treatment of ZnO with Lithium-Potassium Silicate

	Ingredient	Parts by Weight	Remarks
(A)	LiOH	24.2	This combination gives a solution at 31% solids with mole ratio 3.3 (31 Li 3.3). See Appendix II for explanation.
	SiO_2 (from silicic acid or 5-50 nm powder)	100	
	H_2O	248	
	H_2O	210	10% solution 10 li 3.3

Ingredient	Parts by Weight	Remarks
Potassium Silicate Solution (35 K 3.3)	100	Commercially available (Philadelphia Quartz, Sylvania Electronic Products). Dilution gives 10 K 3.3
H_2O	250	

(B) Procedure.

Add 248 parts of water followed by 24.2 LiOH, while mixture is under agitation. Once a solution has been obtained slowly add 100 parts of colloidal silica or silicic acid (85% SiO_2), and blend vigorously until a solution is formed. Dilute to 10% solids with 210 parts of water. In a separate container, dilute the potassium silicate as shown in the schedule to 10%. While a portion of 10 K 3.3 is being stirred, slowly add an equal portion by weight of the 10 Li 3.3.

(C) Store in unplasticized polyethylene or propylene containers.

V. Paint Formulations

Ingredient	Parts by Weight
(A) OI-650 B	10
(B) Dioxane	50
(C) Pigment (see below)	40
(D) Cr_2O_3 (optional, depending on the α desired)	0-1

(E) Pigment Identification

    (a) Sodium silicate treated ZnO, MSA-90

    (b) Lithium-Potassium silicated treated ZnO, MSA-82

    (c) Chrome oxide green with either treatment of ZnO, MS-93

VI. Preparation of Treated ZnO Paints

(A) Dehydration of Pigment. The preferred method of dehydration is by means of microwaves. A slurry is poured into an improvized Teflon

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liner covering a glass container to a thickness of 1/2-1 centimeters. Because power and efficiency may vary between ovens, timing is best judged by heating until the pigment is friable. Normally, a batch based on 454 gms of zinc oxide will require about 40 minutes for dehydration when carried out in two stages. Stage drying is not uniform. After 1-2 minute intervals the treated pigment is turned over. Dehydration must be carried out just prior to use; if stored, the pigment should be redehydrated prior to use to benefit shelf-life of the paint. An alternate and not recommended procedure for dehydration, forced convection oven drying, is messy, time-consuming, and causes separation between pigment and silicate solids. Slow pre-drying at 50-70°C with occasional mixing is helpful until water is gone; next, the temperature is raised to at least 120°C for up to two weeks or so, depending upon attentiveness to the uniformity of dehydration.

(B) Grinding the Pigment. To facilitate spraying, it may be necessary to grind the pigment from (A) in a jar mill. Grinding is accomplished by first pre-slurrying the pigment with 200 proof ethyl alcohol prior to changing into a dry jar mill: rehydration must be eliminated if possible. After milling is accomplished, the pigment is heated over the range of 70-120°C to first eliminate alcohol and finally water. If grinding is carried out at normal speeds, say in a two quart jar with one half inch balls driven at the factory designed rate, an aluminum jar and balls are recommended. Under these conditions, milling longer than twenty (20) minutes is not recommended because ZnO is a soft pigment and as a result subject to discoloring, usually to a shade of yellow. Careful dehydration using microwaves eliminates the need for ball milling.

(C) Dissolving the Resin. Solvating the OI-650 B is accomplished quickly by swirling 10 parts of resin with 10 parts of dioxane in a glass container.

(D) Blending Procedures.

    (a) Mixing is accomplished with minimum fuss by adding 20 parts by weight of the above stock resin solution to a blender followed by 40 parts of dioxane. Next 40 parts by weight of the freshly prepared pigment is slowly added and ground by blender for up to 20 minutes until a dispersion is obtained. The paint is now ready for application.

    (b) Alternatively, the remaining 40 parts by weight of dioxane are added to a blender jar followed by the 40 parts of freshly prepared

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pigment. Additional solvent may be added, but only if the blender motor is laboring during the wetting in. In a separate jar is placed the 20 parts of 50% resin solution. While blending, the dioxane-pigment slurry is slowly added to the resin solution. After this addition is completed, slowly blend for a couple of minutes. The paint is now ready for application.

(E) To tint with Cr_2O_3, modify the a/e ratio, the addition may be made while mixing pigment and resin in the blender. Compensation in weights need not be taken into account because the level of Cr_2O_3 is normally small. Because the tinting strength of Cr_2O_3 may vary, it is recommended that users determine their level to meet a specified solar absorptance. Table 4 in "Formulating Procedures" may serve as a guide.

VII. Preparation of Leafing Aluminum and Black OI-650 B Paints

Ingredient	Parts by Weight
(A) OI-650 B	10
(B) Dioxane	50
(C) Pigment	
(a) Leafing Aluminum MD-5100	10
or	
(b) Carbon Black 999	3

VIII. Application Procedures

(A) Painted Surfaces

1. Abrade surface with 180 grit paper till surface is dull. If evidence of contamination is noted, abrade till metal surface is exposed.

2. Wipe clean with cloth dampened with alcohol.

3. Use Model #18 Binks pressure pot gun. Avoid dry spray.

4. Air supply: Dry nitrogen preferred, or filtered compressed air.

(B) Aluminum and Mild Steel (Preferred Method)

    1.   Abrade surface via sand blasting.*

    2.   Clean with isopropyl alochol and dry.

(C) Stainless Steel

    1.   Sand blast (preferred) or abrade using 80 grit silicon carbide paper.

    2.   Rinse with isopropyl alcohol and wipe dry.

(D) Copper (No alternate method may be used)

    1.   Abrade with 180 grit silicon carbide paper or sand blast.

    2.   Remove grit with water wash.

    3.   Etch surface with 5-7% glacial acetic acid solution or 5-7% citric acid solution. Three minute etch is recommended.

    4.   Rinse with isopropyl alochol and wipe dry.

(E) Epoxy Fiberglass

    1.   Abrade with 180 grit silicon carbide paper until a rough surface rich in fiberglass is exposed.

    2.   Clean debris off with isopropyl alcohol.

    3.   Bake out at 50-60°C long enough to drive off residual solvent.

IX.   Cleaning and Handling

These painted surfaces, as well as any painted surface, should never be handled by bare hands. Abrade any dirty surface that should appear. If much paint has to be removed to accomplish this, then touch up must follow after the debris has been removed.

X.   Touch Up

(A) Abrade with 180 grit silicon carbide paper to bare surface.

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*When sand blasting is not practical, "Scotch Brite" or silicon carbide paper can be employed.

(B) Clean with toluene.

(C) Rinse with isopropyl alcohol.

(D) Touch up as required.

XI. Protection

Polyethylene bagging or wrapping may take place after one week air dry at room temperature or a one hour bake at 120°C. However, since polyethylene films may have organic processing agents, it is recommended that routine cleansing using ethyl or isopropyl alcohol be employed. Dry thoroughly before using.

XII. Shelf Life

The shelf life of all OI-650 B paints is limited. Those using treated zinc oxide may be sprayable for a period of up to eight hours, including blending time: A pot life of 8 hours can be assured for the heated ZnO paints only if instructions are closely followed. Normally the useful lifetime of the resin is extended by refrigeration; the same procedure applies to paints.

A BRIEF DESCRIPTION OF THE CHARACTERIZATION
OF SILICATE SOLUTIONS

Of the raw materials used in the manufacture of alkali-metal silicate solutions, an alkali-metal hydroxide and silica, only the latter can be considered as it is, namely SiO_2. Because strong bases are reactive toward atmospheric constituents such as carbon dioxide and water, their characterization with respect to the cationic equivalent in a known weight or on a mole basis must be as M_2O. The oxide content in a mixture of alkali-metal carbonate and hydrate is obtained gravimetrically after heating.

Processing together M_2O and SiO_2 using heat, and sometimes pressure as well, to give an alkali-metal solution yields a composition difficult to characterize. The simplest description is, therefore, one based on the weights SiO_2, M_2O, and water.

In practice it is customary to express these numbers as the ratio of SiO_2 to M_2O either on a weight or mole basis, and include the water by expressing the solids in solution as a percentage. The lithium and potassium-silicate solutions on pp. 26-27 of Appendix I serve as an example. Lithium hydroxide is a starting material, but to calculate mole ratio and percent solids in the final solution

$$2 \text{ LiOH} \quad = \quad Li_2O \quad + \quad H_2O$$
$$MW = 24 \qquad MW = 30 \qquad MW = 18$$
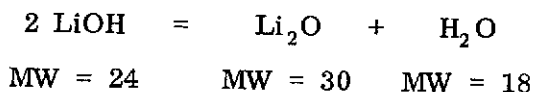
and 48 parts by weight of lithium hydroxide is equivalent to 30 parts by weight of lithium oxide plus 18 parts by weight of water, which must be included in with the added water before a percent solids can be calculated.