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MODULE DEGRADATION CATALYZED BY METAL-ENCAPSULATION REACTIONS

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Four major properties are considered to be relevant in determining service life of a photovoltaic module:

(1) Mechanical: creep resistance, modulus, tensile strength.

(2) Optical: integrated transmission at 0.4 to 1.1 m wavelength.

(3) Chemical: inertness with respect to metals and other components, retention of stabilizers, etc.

(4) Electrical: maintaining effective isolation of conductive components.

These properties were measured after exposing polymer specimens to three types of accelerated stress: thermal, ultraviolet radiation and metal catalysts. These conditions give rise to a large number of complex interrelated free-radical reactions that result in the deterioration of polymeric materials.

In all experiments the data were plotted as log % property retained versus time, to yield generally useful graphs of material behavior. The first property to show change is color (yellowing), determined quantitatively by spectroscopy as a percentage of transmittance (T) at 400 nm. The total optical transmittance, however, retains a surprising high value (400 nm to 1100 nm), even with severe yellowing. Specimens retaining only 10% of the original transmittance at 400 nm were still found to have 74% total integrated transmittance. The mechanical properties during aging were, for the most part, unaffected. When physical deterioration was observed, the decrease in elongation at break was the first characteristic to change, followed by the decay of tensile strength. The dielectric strength was found to be the least variable of the properties measured; it retained 100% of the control values in all but the most extreme cases of degradation.

Thermal aging was conducted in the dark in atmospheres of air and nitrogen at temperatures of 60°C, 85°C, 105°C and 130°C. Results show that the candidate pottants have very good thermal stability, with no life-limiting degradation occurring at 105°C.

For the purposes of this discussion only the data on metal-catalyzed reactions on EVA A-9918 will be presented. All of the other encapsulants tested behaved in a similar or worse manner. The EVA A-9918 consists of five parts: (1) ELVAX 150, the encapsulant; (2) Luprasol 101, the curing agent;

(3) Cyasorb 531, an ultraviolet screen; (4) Naugard P, an antioxidant, and (5) Tinuvin 770, an ultraviolet stabilizer. This material was developed by Springborn Laboratories, Inc., under contract to JPL and is available to the industry.

Metal-catalyzed oxidation in the presence of copper was discovered to be the most severe condition examined. The EVA was molded around copper screens and the color (% T at 400 nm) measured after periods of thermal soak at 105°C. The material was found to degrade rapidly and reached end of life at 400 hours. Specimens that had been treated with silane primer demonstrated improved performance and the induction period (before rapid degradation) was moved out to beyond 1000 hours. Similar catalytic reactions have been observed with both Ti^{+2} and T^{+3} ions but no reactions have been observed with aluminum, silver, nickel or 60-40 solder up to 1000 hours of 105°C thermal tests.

The postulated mechanisms for the general case and for the metal-catalyzed specific case are:

A. The general case:

INITIATION $R\text{-}R \xrightarrow{\Delta} 2R\bullet$ (1)

The breaking of the R-R bond to form the R• free radical is a slow reaction. This step, which requires 80 kcal/mol of energy to break the bond, corresponds to the induction period. Energy can be supplied by heat or light and the unpaired electron in the R• complex can react with oxygen and/or with some metal complexes.

PROPAGATION $R\bullet + O_2 \longrightarrow ROO\bullet$ (2)

$ROO\bullet + RH \longrightarrow R\bullet + ROOH$ (3)

The formation of the R in reaction (3) shows this propagation step is autocatalytic and the change in slope of the curves shows it to be quite fast. The formulation of ROOH hydroperoxide is the operative mechanism that allows for redox reactions with multivalent metals to accelerate the production of free radicals and make the system autocatalytic.

B. The metal catalysis case:

$ROOH + M^{n+} \longrightarrow M^{(n+1)} = OH- + RO\bullet$ (4)

$ROOH + M^{(n+1)} \longrightarrow M^{n} + H^{+} + ROO\bullet$ (5)

to give a summary reaction of

$$2ROOH + \xrightarrow{Cu^{+2}/Cu^{+3}} RO + ROO\bullet + H_2O$$

This reaction is quite fast and, as can be seen from the reaction products, is autocatalytic.

General conclusions that can be reached are:

(1) The first quantifiable property to change is color.

(2) Observed degradation mechanisms are of the induction-period type.

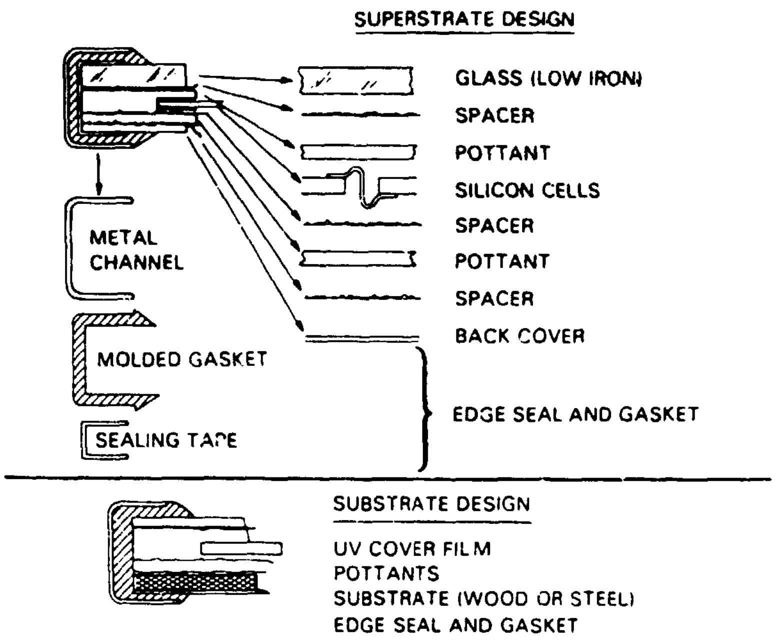
(3) Higher acceleration rates are required to assess formulation changes in less time.

(4) Not all metals catalyze degradation mechanisms; copper and titanium do, but aluminum, silver, nickel and 60-40 solder do not.

(5) Silane treatment has extended the induction time before autocatalytic degradation but exact formulations for long life have not yet been found.

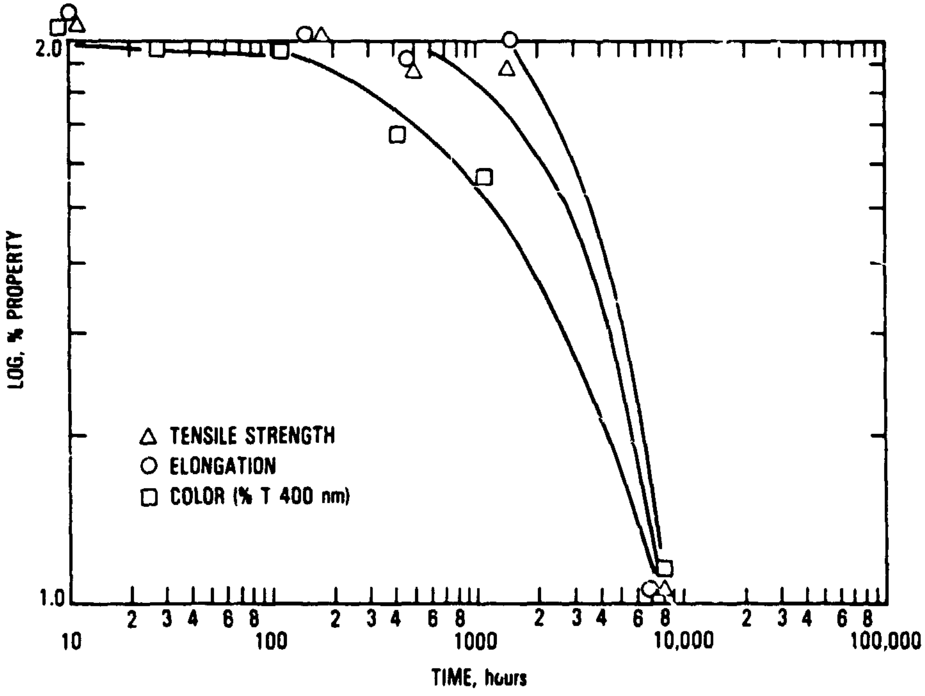
These studies, sponsored by the U.S. Department of Energy through the Jet Propulsion Laboratory, were carried out at Springborn Laboratories, Inc., under the direction of Paul Willis.

Module Designs



Thermal Aging

EVA A9918—130°C



- **No change in optical, mechanical, or electrical properties after:**

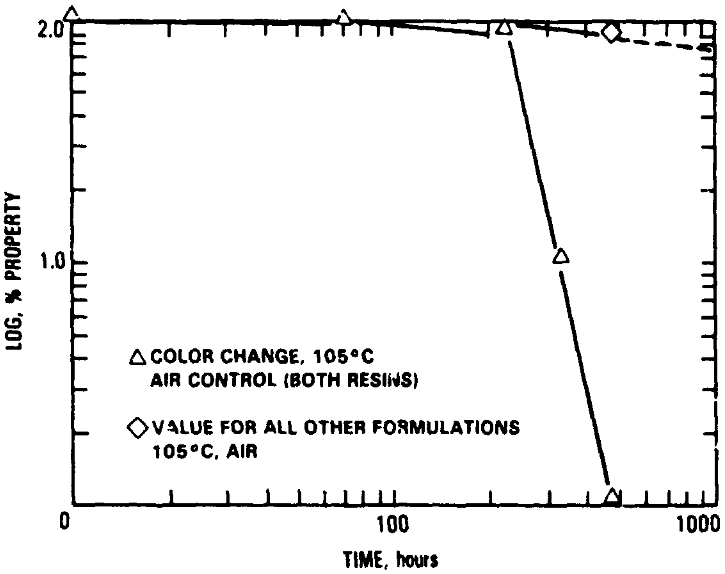
90°C: 7200 hours 105°C: 1000 hours

Metal Deactivation Experiments

- **Prepare polymer formulations 0.2 phr deactivator**
- **Mold over copper screen**
- **Copper: silane / no silane treatment (Z-6030)**
- **Thermal age, air and nitrogen**
- **Monitor % T 400 nm (yellowing)**

Metal Deactivation

(COPPER SCREEN)
EVA A9918



- **EVA controls degraded at 400 hours (coloration and flow of resin away from copper screen)**

Metal-Catalyzed Degradation

Copper and possibly other multivalent metals accelerate oxidation reactions in polymers "pro-oxidants"

General Mechanisms:

- **Initiation:** $R - R \xrightarrow{\Delta} 2\,R\cdot$
- **Propagation:** $R\cdot + O_2 \longrightarrow RO_2\cdot$
  $RO_2\cdot + RH \longrightarrow R\cdot + ROOH$
- **Metal catalysis:**
  - **Multivalent metals complex hydroperoxides. React through redox mechanisms, accelerates production of free radicals**

$$ROOH + M^{n+} \longrightarrow M^{(n+1)} + OH^{-} + RO\cdot$$
$$ROOH + M^{(n+1)} \longrightarrow M^{n} + H^{+} + ROO\cdot$$

  - **Soluble ions are catalytic. Affect propagation rate only.**

Sum:

$$2\,ROOH \xrightarrow[(FAST)]{Cu^{+2}/Cu^{+3}} RO\cdot + RO_2\cdot + H_2O$$

Conclusions (Results to Date)

General Observations

- **First property to change: color (yellow)**
- **Degradation: predominantly induction period type, few first order**
- **Exposure times are long, need higher acceleration to assess formulation changes in less time**

Metal Activation

- **Avoid metallic copper in contact with pottant (other multivalent metals?)**
- **No reactions observed with aluminum, 60/40 solder**
- **Wash off solder flux (acidic residues, soluble ions)**
- **Deactivators give improvement (effectiveness?)**
- **Silane gives improvement (effectiveness?)**

DISCUSSION

SOMBERG: I know that at least one of the modules you showed has not been made for at least three years. Are those typical of all the tests that have been run that you have described?

MON: Initially all we had was Block I, II and III modules, some of which are no longer made. Then we started with Block IV and we are in the process of getting our hands on Block V modules, to put in these chamber too.

SOMBERG: Would you say that the data you have shown are really of Block III and before that?

MON: For the most part, yes. We have had enough time. We have been running Block IV stuff now for about 100 days, if I recall -- well, probably longer than that, since late 1982. About seven months.

SOMBERG: What does that look like?

MON: About as bad as the first group. About as bad as the first three Blocks.

SOMBERG: How many different module manufacturers are in that test?

MON: All the major ones.

SOMBERG: So you are saying Block IV looks about the same as Block III?

MON: Well, yes. When you ask me a question like that, how am I supposed to differentiate between modules that look like this when they all begin to look like this after 70 days and the 85-85 chamber? Yes. EVA is about as bad as PVB as far as degradation is concerned. We are talking about encapsulations rather than metallizations. EVA yellows severely. Especially when in contact with silver metallization. More than PVB, I would think. Maybe not; it is hard to say. The best insulation, from the observations that I see here, is the old silicones. They seem to be much better.

SOMBERG: What about the Block IV cells. What do they look like compared -- not the encapsulation, but the cells themselves. Are you saying that the problem in Block IV appears to be about the same as it was in Block III?

MON: I can't say that.

SOMBERG: Are there any initial indications that it appears that way?

MON: Oh, yes. Like I say, the cells themselves --

SOMBERG: Not the encapsulation of the cells.

MON: No. I haven't seen the cells.

ROYAL: There is another group that is testing cells, with a slightly different approach. The data are not available in that exact same format.

LIVESAY: Have you had the chance to look at that blossoming or that pattern under a scanning electron microscope?

MON: Yes. We are doing that now. What we have discovered there is a lot of silver concentration, of course, right on the metallization. As you probe beyond the metallization, the concentration goes down and as you probe in a lateral direction, the metallization, the silver content also goes down. There is definitely a diffusion.

LIVESAY: What is the microstructure? I have seen things like this, sometimes they are a whisker growth and other times they are dendritic patterns. Do you see that kind of thing?

MON: The microstructure, first of all you see what looks like white puff balls, and stars, and this is formed in the encapsulation but it is right above the metallization. So again that is probably a metallization-catalyzed type of reaction. There seems to be a dark area just off the end of the metallization. There seems to be very little silver content there when we probed for that. It seems to be beyond that. I'm not sure I understand it. It is not doing any quantum jumping as far as I can tell.

QUESTION: There was silver and there is no longer silver?

MON: When you peel the encapsulation off, you can look and see part of the metallization and the blossoming in the encapsulation, and the cell for all apparent purposes is as good as the day it was delivered except that there is probably less silver because we do a dot scan with the EDAX and get a dot map and you can see silver in a decreasing diffusion-like pattern.

WOLF: But you lost silver there?

MON: That's right.

SCHWUTTKE: It would be a migration problem. You have an electromigration problem.

MON: That is correct.

STEIN: Would you clarify that just a bit more? Would you say that the polymer, the encapsulant, is acting as an electrolyte in this case?

MON: Remember, these have been in a humidity chamber.

STEIN: I understand that. If the humidity is absorbed by the polymer then you find silver in the polymer.

MON: That is correct. My interpretation of this is that water vapor has penetrated the encapsulation and has caused it to become an electrolyte. This happens under the influence of the electromotive forces, as you can see by the bending at the tips, and it is electroytic.

WEAVER: We observed on the PVB encapsulant that it occurred all along the whole collector bar; it occurred in a very short period of time. We installed those last June, but our first cold night with high humidity was in late October, and within one week it showed up. It has not gotten any better or worse since then.

MON: We don't know how long it took for this to occur but this residence has only been powered by solar for about a year.

WEAVER: In my discussion with Neal Shepard, when I called his attention to our problem, he said it occurred very quickly both at the Southwest and the Northeast Residences in a very short period of time. All of a sudden it was there.

MON: This is the Southwest right here.

STEIN: I would suggest that the resistivity of the encapsulant at different relative humidities and temperatures might be a very significant factor here, and should be a means of choosing appropriate materials. If that drops too much, at 85°C or even 100°C, you are in trouble.

MON: Well, we never know these modules in operation will be at around 60°C, the cell temperature, so we are doing accelerated testing and I think we will still be in trouble because I think that the 85°C/85% RH test for, say, 90 days corresponds to probably less than 20 years, in fact I did a back-of-the-envelope calculation one time and it looked like 12 to 15 years.

WEAVER: The concern about high temperature can be brought further forward when you say if I have a weak cell, its temperature will go well beyond 65°C. You will get cells up close to 100°C; if it is a bad cell then you will start heating everything around it.

MON: That right. There will be a reverse bias.

HORN: We've done work where we've seen a similar phenomenon when we do electrostatic-field-assisted bonding of borosilicate glass to a cell. Where we have the glass under high temperature and voltage gradient through the glass and we see a browning halo over the contact grid in the glass. We have actually done analyses of this and it has shown that it is silver migrating into the glass. We have postulated that it is an ion exchange between the sodium in the glass and the silver. By depositing just a few hundred angstroms of SiO_x through a shadow mass down to that grid line we can eliminate the problem. It might be as simple as putting the AR coating over the contact grid except where you want to make the contact.

MON: Do you have literature on this?

HORN: We published last fall in the IEEE PV Specialist Conference.

MON: I would like to get together with you and get that reference.

WONG: I have two short questions related to this. The first question is, is this blossoming effect happening only under the high humidity and heat condition?

MON: That is correct. Except that we have seen it in the Southwest RES and in various field sites at so called normal field temperatures.

WONG: The second question is, you say the water acts as an electrolyte. Do you mean that the silver will be dissolved in the water, through the water and then deposit at the low potential region?

MON: No, I won't go so far as to say that because I haven't observed that yet. All I am saying is that basically, from that previous picture, it is my contention that it is probably an electrolytic phenomenon. Whether it is actual silver ions or some sort of a -- it could be an electrophore type of thing too, I am not sure that is what you call it. You have a situation where you have either an ion or a polarized molecule following the field line. There is a name for that and I can't remember what it is. But I don't know yet what the mechanism is.

WONG: But it has to be something dissolved in water that can transport through the water. A possible low potential field.

MON: I am sure of that.

WONG: And the driving force has electrochemical potential, do you think?

MON: Yes. I have not seen any deposits on the cathodes. We are looking for that but we haven't seen it. But by the time it gets -- like this gap -- it isn't much of a gap -- but this particular module was accelerated at the difference between those two cells, which is 17 volts. This took 1700 hours, roughly, in that time frame, for this one to turn. So again, I don't know what this translates into in real field conditions. But I do think it is electrolytic. I can't prove it yet.

AMICK: Which is the positive and which is the negative?

MON: The positive one is the bottom one, the one that has the blossom on it.

AMICK: So that is the one where hydrogen would come out if you were electrolyzing the water.

MON: That is correct. This is the cathode.

AMICK: So that is where oxygen would come out? And if oxygen comes out--

WONG: Did you see any bubbles or pockets or oxygen gas in this?

MON: No.

COMMENT: Do you know when Paul (Willis) will be able to make tests with voltage applied?

GALLAGHER: I can't answer that question but I think it is only a matter of time until he is instrumented to do it. I think one of the things that has come out of my being here is my awareness of the fact that the phenomena that we just heard of are very much accelerated by voltage.

COMMENT: Or maybe retarded.

GALLAGHER: Again, there is an activation energy of some sort involved, either positive or negative. Any other questions?

AMICK: Brian, you really should be looking at them in light, too at air mass.

GALLAGHER: I agree, there is another way of looking at this. If you look at the metallic systems that are available, and what Paul (Willis) found: sort of an accidental thing, and he went after it to see what was causing it. Normally one wouldn't worry about the copper if you had the data on nickel because in the course of producing the copper-plated structure it would be very easy and quite economical to give it a nickel flash before you remove it from the plating system, so you wouldn't go after it this way. What happened was that he found a phenomenon he got interested in, and he went after that phenomenon, and then once he started reporting on it he got pushed a little bit to look at some of the other metals to solve it in a different way. He, being a chemist, and very interested in polymers, wants to use that approach, wants to deactivate whatever the metal is in a chemical reaction. In our case, we would just replace the copper with nickel and not worry about it. But you are right, the acceleration factors, now that we know they are present, should be used.