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INVESTIGATION OF TEST METHODS,
MATERIAL PROPERTIES, AND PROCESSES
FOR SOLAR CELL ENCAPSULANTS

JPL Contract 954527
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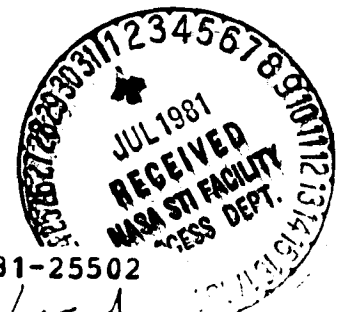
ENCAPSULATION TASK OF THE LOW-COST
SILICON SOLAR ARRAY PROJECT

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, by agreement between NASA and DOE.

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I. SUMMARY

Springborn Laboratories is engaged in a study of evaluating potentially useful encapsulating materials for the Low-Cost Silicon Solar Array project (LSA) funded by DOE. The goal of this program is to identify, evaluate, and recommend encapsulant materials and processes for the production of cost-effective, long-life solar cell modules. During this quarter, the development of pottant compounds was emphasized.

Formulation of the Butyl acrylate syrup/casting pottant was completed and is now ready for the first stage of industrial evaluation. The formulation contains an ultraviolet stabilizer system and may be cured with an initiator that, unlike former selections, presents no shipping or handling hazards to the user. The catalyzed syrup is stable at room temperature and has a pot life of at least an eight hour (one shift) period of time. The syrup cures to a transparent rubber in 18 minutes at a temperature of 60°C.

The formulation of the ethylene/methyl acrylate lamination pottant was also completed during this period of time. This compound is the alternative pottant to EVA and is similarly produced as an extruded sheet that is wound into rolls. Experiments were conducted to select the most appropriate base resin for this compound and generate a first-cut formulation suitable for industrial evaluation purposes. The large scale extrusion conditions were determined and a 250 pound quantity was produced as a film of 30 inch width and 0.02 inch gauge. This resin is inherently non-blocking consequently no release paper was used to separate the plies. Experimental modules were prepared to verify performance and the cure profile was determined at a variety of times and temperatures.

Due to the current commercial interest in the EVA lamination pottant some revised studies were conducted with respect to the time/temperature cure requirements for successful use of this compound. The times needed to produce successful gel contents were redetermined at a variety of temperatures and these results were related to the peroxide half-life temperature curve.

II. INTRODUCTION

The goal of this program is to identify and evaluate encapsulation materials and processes for the protection of silicon solar cells for service in a terrestrial environment.

Encapsulation systems are being investigated consistent with the DOE objectives of achieving a photovoltaic flat-plate module or concentrator array at a manufactured cost of \$0.70 per peak watt ($\$70/m^2$) (1980 dollars). The project is aimed at establishing the industrial capability to produce solar modules within the required cost goals by the year 1986.

To insure high reliability and long-term performance, the functional components of the solar cell module must be adequately protected from the environment by some encapsulation technique. The potentially harmful elements to module functioning include moisture, ultraviolet radiation, heat build-up, thermal excursions, dust, hail, and atmospheric pollutants. Additionally, the encapsulation system must provide mechanical support for the cells and corrosion protection for the electrical components.

Module design must be based on the use of appropriate construction materials and design parameters necessary to meet the field operating requirements, and to maximize cost/performance.

Assuming a module efficiency of ten percent, which is equivalent to a power output of 100 watts per m^2 in midday sunlight, the capital cost of the modules may be calculated at \$70.00 per m^2 . Out of this cost goal only 20 percent is available for encapsulation due to the high cost of the cells, interconnects and other related components. The encapsulation cost allocation^a may then be stated as \$14.00 per m^2 which includes all coatings pollutants and mechanical supports for the solar cells.

Assuming the flat plate collector to be the most efficient design, photovoltaic modules are composed of seven basic construction elements. These elements are (a) outer covers; (b) structural and transparent superstrate materials; (c) pollutants; (d) substrates; (e) back covers; (f) edge seals and gasket compounds, and (g) primers. Current investigations are concerned with identifying and utilizing materials or combinations of materials for use as each of these elements.

a. JPL Document 5101-68

Extensive surveys have been conducted into many classes of materials in order to identify a compound or class of compounds optimum for use as each construction element.

The results of these surveys have also been useful in generating first-cut cost allocations for each construction element, which are estimated to be as follows (1980 dollars):

Construction Elements	Approximate Cost Allocation ^{d.} (\$/m ²)
. Substrate/Superstrate (Load Bearing Component)	7.00
. Pottant	1.75
. Primer	0.50
. Outer Cover	1.50
. Back Cover	1.50
. Edge Seal & Gasket	1.85

d. Allocation for combination of construction elements: \$14/m².

From the previous work, it became possible to identify a small number of materials which had the highest potential as candidate low cost encapsulation materials. The following chart shows the materials of current interest and their anticipated functions:

Candidate Encapsulation Materials

<u>Load Bearing Component</u>	<u>Pottants</u>	<u>Cover Films</u>
Superstrate Design:		Back Covers:
. Soda-Lime Glass	. Ethylene/Vinyl Acetate	. Mylar
	. Ethylene/Methyl Acrylate	. Tedlar
Substrate Design:	. Silicone 534-044 (GE)	. Aluminum Foil
. Fiberboard	. Poly-n-Butyl Acrylate	. Other Metal Foils
. Flakeboard	. Aliphatic Polyurethanes	
. Mild Steel		Outer Covers:
. Glass Reinforced Concrete	(For use in both substrate and superstrate designs.)	. Tedlar 100 BG 30 UT
		. 3M X-22417

Recent efforts have emphasized the identification and development of potting compounds. Pottants are materials which provide a number of functions, but primarily serve as a buffer between the cell and the surrounding environment. The pottant must provide a mechanical or impact barrier around the cell to prevent breakage, must provide a barrier to water which would degrade the electrical output, must serve as a barrier to conditions that cause corrosion of the cell metallization and interconnect structure, and must serve as an optical coupling medium to provide maximum light transmission to the cell surface and optimize power output.

This report presents the results of the past quarter which has been directed at the continuing development and testing of pottants.

The topics covered in this report are as follows:

1. The development and final formulation of the butyl acrylate syrup/casting pottant. Emphasis was placed on developing a system with long pot life, room temperature stability and rapid cure at reasonably low (50°-60°C) temperatures. Low hazard initiators were evaluated for these characteristics without presenting the danger of violent decomposition, fire, and the necessity for refrigerated storage required with previously selected peroxides. Time/temperature cure requirements were determined for completed formulations prepared with ultraviolet stabilizers.
2. Ethylene/methyl acrylate base resins were explored for suitability in producing a compound for industrial evaluation purposes. This compound contains an antioxidant and a synergistic combination of ultraviolet stabilizers to extend its service life under outdoor exposure conditions. Peroxides used to cure the resin were also screened and a good first candidate was selected. The extrusion and processing conditions of this film lamination pottant were determined using a 2 1/2 inch pilot plant extruder and material was prepared for industrial evaluation.
3. Due to the current interest in the EVA pottant compound that has been produced at Springborn Laboratories, additional studies were conducted to confirm the cure behavior and the time/temperature requirements resulting in acceptable levels of gel content (measure of cure). A time/temperature gel content table was developed and a revised cure curve prepared to assist manufacturers with processing requirements. This curve relates well to the half-life decomposition curve of the peroxide curing agent.

III. POTTANTS

Pottants are the rubbery transparent materials which serve as the encapsulation medium directly in contact with the solar cell. The required properties of the pottant are transparency, thermal stability, UV resistance, low modulus for stress relief, the ability to be crosslinked (for thermal creep resistance), and others. In addition to these performance properties the pottant must be able to be used in some fabrication scheme for the preparation of solar modules without damage to the cells, interconnects or other components. Investigations by Springborn Laboratories into materials suitable for pottants also necessitated the examination of possible processing and fabrication techniques. Two methods evolved from these studies, lamination and casting. Lamination concerns the preparation of a sandwich composed of the pottant and other components in sheet form which are then fused under heat and vacuum to give the completed module. Casting involves the use of a liquid pottant which is pumped into a cavity containing the other components. After filling (and heating in some cases) the pottant sets to a solid compound and develops its final cured properties.

In addition to the reevaluation of the cure behavior of the EVA lamination pottant, this quarter has emphasized the completion of an ethylene/methyl acrylate resin based lamination pottant and a butyl acrylate based syrup/casting pottant.

Butyl Acrylate Syrup

Previous efforts^a concerning the development of pottants have been aimed, in part, at the formulation of an all acrylic casting syrup based on butyl acrylate, a transparent monomer/polymer liquid.

The polybutyl acrylate pottant was originally investigated at JPL and found to be a desirable material for use as a pottant for reasons of its physical properties and also its photostability. A study of the photochemistry indicates that poly n-butyl acrylate (cured) forms a stable

a. Willis, P. and Baum, B., Investigation of Test Methods, Material Properties and Processes for Solar Cell Encapsulants, Eighteenth Quarterly Report to Jet Propulsion Laboratories, Contract #954527, Springborn Laboratories, Enfield, Connecticut, September 1980.

crosslinked network that undergoes chain scission and crosslinking at equal rates when exposed to ultraviolet radiation in the photoactive regions of the spectrum^a. Study of the wavelength dependance of the photodegradation of the polyacrylates shows that photoreactivity continues up to 310 nm, only barely into the solar spectrum. This indicates that the acrylic elastomer will require less stabilization than materials with strong absorptions that may also reach far into the terrestrial ultraviolet^b.

The compound originally prepared by JPL was composed of a premade butyl acrylate polymer that was then dissolved in a quantity of monomer to yield a pourable syrup. This syrup was then cured by heating in the presence of a free radical initiator. The cured material produced by this method is a water-white highly transparent elastomer of low modulus.

The difficulty experienced with early formulations was that of high cure temperature, long cure times and low gel contents.

Subsequent work concerned the modification of this base formulation with functional crosslinking agents to reduce the cure time/temperature and raise the gel contents. A successful formulation was discovered and a composition resulted that demonstrated a 68% gel content with complete cure of the syrup after one hour at 60°C. The new syrup constitutes the base formulation on which all subsequent work has been based and has the following composition:

Butyl Acrylate Monomer	60%
Butyl Acrylate Polymer	35%
1, 6-Hexanediol Diacrylate (Springborn No. A12805)	5%

This material achieves cure after mixing with an appropriate initiator and then heating for the required period of time. The best results were achieved with the addition of 0.5% by weight of Lupersol -11^c, which resulted in a 87% gel content after one hour at 50°C.

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- a. Gupta, A., Photodegradation of Polymeric Encapsulatiants of Solar Cell Modules, LSA document 5101-77, 8/10/78, Jet Propulsion Laboratory, Pasadena, California.
 - b. Morimoto, K., and Suzuki, S., Journal of Applied Polymer Science, 16, 2947, (1972).
 - c. Lupersol -11 is t-Butyl Peroxypivalate, 75% in mineral spirits.

Further experiments were conducted on cure systems for the polybutyl acrylate pottant system with the hope of finding a room temperature cure chemistry that would remove the need for oven heating after module fabrication. The experiments involved polymerization of the syrup at lower temperatures, the screening of lower temperature catalysts and the use of "promoters" that cause the cure reaction to procede at a faster rate. A number of systems were found to give a wide range of time/temperature conditions resulting in good cure of the syrup. The results of these experiments are summarized in Table 1 in the appendix.

As may be seen from an examination of the table, a wide variety of pot lives, cure temperatures and cure times are available for use with this resin system. Probably the most useful cure systems are those based on Lupersol - 11, both promoted and unpromoted. Mixed syrup/catalyst formulations do not appear to cure under room temperature conditions, therefore may be used for fabrication during an eight hour shift; however they can be cured fairly rapidly at low (35°C) temperatures after the module has been filled with the syrup. The use of a promoter, stannous octoate, permits the cure to take place as low as 35°C and, at higher temperatures, cuts the cure time by approximately 1/2 when compared to the unpromoted system. The other initiators investigated Lupersol - 225, Benzoyl peroxide and Vazo - 33W, are either ineffective, cure too slowly or cure too rapidly with a short room temperature pot life. Lupersol - 11 is the best selection between these extremes. It also results in slightly improved physical properties over the others, as is seen in the following table:

Polybutyl Acrylate Pottant
Cured Properties vs. Initiator System

Initiator	Level %	Cure Time ^a (min)	Cure ^b		
			Temperature °C	Strength (psi)	Elongation (%)
Benzoyl Peroxide	0.5%	60	60	138	50%
Benzoyl Peroxide	0.1%	180	60	181	100%
AIBN	0.5%	60	60	267	100%
Lupersol-11	0.5%	180	50	202	100%
Vazo 33W	0.5%	60	25	138	74%
Vazo 33W	0.1%	60	25	91	55%
Vazo 33W	0.5%	60	25	99	63%
Stannous Octoate	0.1%				

- a. Minimum time permitted, cure may have taken place in much shorter time.
b. Temperature at which polymerization initiated, does not include exotherm.

In general, it has been found that the butyl acrylate syrup pottant is a useful and rapid curing casting syrup that may be initiated using a wide variety of initiators and time/temperature requirements. There is some dependence on physical properties and the type of initiator used. The higher temperature cure systems appear to result in slightly higher elongations and noticeably better tensile strengths.

Despite the apparent success with this formulation, the study of initiators had to be extended. Lupersol-11 (Lucidol Corporation, Buffalo, New York) requires refrigerated shipment and is classified as a "deflagration hazard". This material has a self-accelerating decomposition temperature (SADT) of 85°F (30°C) at which point it undergoes sudden decomposition with the generation of force and/or smoke and fire. Although appropriate for laboratory use, this material may be too dangerous for general industrial application. An alternative was consequently sought.

Aliphatic peroxides were selected from lower hazard categories and screened for efficiency in curing the butyl acrylate syrup pottant, both with and without the presence of the promoter (stannous octoate). The following table records the data obtained on cure times at 60°C with a variety of these safer compounds:

Low Hazard Peroxide Initiators For
Butyl Acrylate Pottant

Initiator	Time to Cure (minutes) at 60°C	
	Butyl Acrylate w/ 0.5% Initiator	Butyl Acrylate w/ 0.5% Initiator and 0.1% Promoter ^c
Alperox-F ^a	18	9
Lupersol 220-D50	NP	NP
Lupersol 256 ^b	13	28
Lupersol 101	NP	NP
Lupersol 130	NP	NP
Lupersol 231	NP	NP

- a. Alperox-F is Lauroyl peroxide, Lucidol Corporation, Buffalo, NY
 b. Lupersol 2, 5 dimethyl -2,5- bis (2-ethyl hexanoyl-peroxy) hexane
 c. Promoter, M&T catalyst Number T-9.

Of the two peroxides that function well as initiators, the first, Alperox-F (lauroyl peroxide) was selected for further use due to its lower hazard rating. This compound falls into the lowest hazard rating of flammable peroxide compounds; "low fire or negligible hazard". It has a self-accelerating decomposition temperature (SADT) of 120°F (50°C) at which point it undergoes slow decomposition accompanied by mild gassing or bubbling. This compound is thermally stable, has no shock sensitivity, decomposes mildly at high temperatures and at Springborn Laboratories constitutes a negligible fire hazard. Flammability tests done with a 5-pound quantity found the material difficult to ignite and maintain burning. Experiments were then performed to assess the efficiency and time/temperature requirements with Alperox-F. The time to cure was determined at room temperature, and two potentially useful fabrication temperatures, 50°C and 60°C. The experiments were run with both promoted and unpromoted butyl acrylate syrup. The following table records the results:

Butyl Acrylate Syrup Number A12805 w/	<u>Time to Cure, Minutes</u>		
	<u>Room Temperature</u>	<u>50°C</u>	<u>60°C</u>
Alperox-F, 0.5%	NP	NP	18
Alperox-F, 0.5% Promoter T-9, 0.1%	NP	25	9

As may be seen, the cure reaction may be conveniently initiated at temperatures as low as 50°C with a promoted system and the mixed syrup does not appear to advance at room temperature. Specimens of mixed syrups were tested for cure after 18 hours at 25°C and were found to cure satisfactorily within approximately 50 minutes at 60°C. The reason for the increased time required cannot be explained at this time.

The last step in the formulation of this syrup to get a product ready for evaluation purposes involved the incorporation of additives to impart further UV/weathering stability to this resin. A survey of the literature resulted in a combination of stabilizers that have been found to be effective in acrylic resins. This combination of stabilizers was subsequently examined for cure compatibility and an additional compound, 5-vinyl tinuvin was included as an absorber capable of reacting in with the syrup during the cure reaction. The results of these formulations appears in Table 2 in the appendix.

The best overall formulation based on clarity, cure requirements efficiency of cure and physical properties was selected from this table and constitutes the first industrially ready compound that will be sampled to industry for evaluation purposes. This material will be produced at Springborn in research quantities under the designation Butyl acrylate, 13870, and will have the following composition:

Formulation Number: 13870

<u>Ingredient</u>	<u>%</u>	<u>Parts</u>	
Butyl Acrylate, Polymer	34.72	35	} 100 parts "resin"
Butyl Acrylate, Monomer	59.52	60	
1, 6-Hexanediol Diacrylate ^a	4.96	5	
Tinuvin-p ^b	0.248	0.25	
Tinuvin 770 ^c	0.0496	0.05	

Alperox-F ^d (initiator)	0.496	0.50	
	<u>99.99%</u>	<u>100.80</u>	

- a. "SR-238", Sartomer Corporation, Essington, PA.
- b. 2(2'-Hydroxy-5-methyl phenyl)benzotriazole, Ciba-Gigy, Ardsley, NY.
- c. Bis(2,2',6,6'-tetramethyl-piperidinyl-4)sebacate, Ciba Gigy, Ardsley, NY.
- d. Lauroyl peroxide, Lucidol Division of Pennwalt Corp., Buffalo, NY.

In use, the formulation is completely compounded with the ingredients shown, except for the initiator (Alperox-F) which is blended into the syrup immediately before use. After mixing the initiator (a white powder) in with the syrup, the mixture is then degassed with stirring under vacuum at room temperature to remove air bubbles that may inhibit the cure and result in voids in the pottant. Alternatively, the initiator may be combined with the base syrup in an airless mixing process. The solid initiator does, however, take a period of time to dissolve (5-10 minutes at room temperature).

As is shown in entry number 11 on Table 2 in the appendix, completely formulated compositions of this syrup are stable for at least a one-day period of time without premature cure occurring and at 50°C the cure time is still in excess of one hour. This characteristic provides for ample pot life and permits the preparation of syrup for an entire day's run to be done

ahead of time. Cure is accomplished easily at temperatures of 60-70°C. The cure time at 60°C has been found to be in the order on nineteen minutes, and at 70°C, about 14 minutes. Higher temperatures would result in further reductions in cure time.

After cure, the material is a transparent low modulus rubber with the following measured properties:

Total integrated transmission, %T (350-800 nm)	89 %
Refractive index, n_D	1.47
Gel content, by extraction	80 %
Volatiles, residual	0.7 %
Tensile Strength ^a	293 psi
Ultimate elongation ^a	110 %
Modulus, Young's or tangent	90 psi

a. ASTM S-638, at 25°C

Measurements are in progress to determine the true engineering modulus (Young's modulus) at low strains for use in module stress calculations.

This pottant has a very high heat of polymerization and generates considerable exotherm when the cure process starts. This accounts also for the rapid rate of conversion. The cure reaction is essentially complete within about 5 minutes after initiation.

A simple calorimeter was used to measure the heat of polymerization developed during the cure reaction. The total heat of reaction was found to be in the order of 77 gram-calories per gram of syrup^a. This is equivalent to approximately 139 BTU/pound and is developed within a ten or fifteen minute period as the cure proceeds. During the cure cycle in fabrication, it would be advantageous to have the modules in such a location that the excess energy from this exotherm may be dissipated (circulating air oven).

Additionally, the fast rate causes thermal stresses in the curing resin and, combined with polymerization shrinkage, may result in the appearance of fractures. These effects do not appear to be troublesome in thin sections (100 mils) where the exotherm is dissipated. Plaques produced in standard molds cure with no difficulty to clear rubbery sheets with slight surface tack.

a. This calculates to approximately -63 KJ mole^{-1} heat of polymerization for pure butyl acrylate. Literature values are: styrene, -69 KJ mole^{-1} , and methyl methacrylate, -58 KJ mole^{-1} .

Springborn Laboratories will be ready to provide samples of the butyl acrylate pottant to industry within the next few months. Pilot plant facilities must be modified for preparation of the syrup on a larger scale before evaluation quantities become available. The required equipment, a wiped film evaporator, has been ordered and the production of industrial evaluation samples of BA 13870 will be started as soon as possible.

Ethylene/Methyl Acrylate

The development work of the past year has emphasized EVA (ethylene vinyl acetate) as the pottant due to its successful performance and its potential for commercial readiness. This modified polymer is available in roll form from Springborn Laboratories for industrial evaluation.

Investigations of pottants as alternates to EVA have been under investigation. These compounds represent "second choice" materials in the event that the EVA pottant appears to be unsuitable for a particular module design or process. These investigations, hopefully, will also result in a few alternate choices of pottant for solar module manufacturers who may be pursuing different fabrication concepts than those emphasized in this report.

The criteria for the selection of alternate pottants are essentially the same for EVA; high transparency, processability, weatherability (or the potential to be made weatherable) and attractive cost.

A resin that appears to be an excellent alternate to the EVA pottant system has been identified^a and during the past quarter has been brought to the stage ready for industrial evaluation.

This new pottant is based on ethylene/methyl acrylate, a random copolymer of ethylene gas and methyl acrylate acrylic monomer. This is a versatile polymer with wide processing latitude, good thermal stability and is less crystalline and consequently softer than polyethylene. Although it has been commercially available in good supply for years, ethylene/methyl acrylate (referred to as EMA) is probably the least known of all of the ethylene

a. Willis, P. and Baum, B., Investigation of Test Methods, Material Properties and Processes for Solar Cell Encapsulants, Seventeenth Quarterly Report to Jet Propulsion Laboratories, Contract #954527, Springborn Laboratories, Enfield, Connecticut, September 1980.

copolymers. EMA is produced in a conventional high pressure reactor in which the methyl acrylate monomer is injected into an ethylene stream in the reactor. Under proper control of pressure, temperature and catalysts, the two polymerize to produce the copolymer. During the polymerization, the methyl acrylate enters the polyethylene backbone to produce side branches that subsequently interfere with the crystal structure inherent to polyethylene and result in the alteration of many properties. These acrylate groups occur at random positions along the backbone of the polymer and in most commercial resins constitute about 20% of the polymer by weight.

The most noticeable changes induced by the presence of the acrylate group are lowering of the melting point (Vicat softening point), reduction in stiffness (modulus), an improvement in stress crack resistance, an increase in the dielectric strength, a decrease in the softness and an increase in the total optical transmission. These properties result in a resin that has potential for use as a solar module encapsulant. A property comparison between EMA and low density polyethylene is shown in the following table:

Property	Ethylene-methyl acrylate copolymer	Low-density polyethylene homopolymer
Melt index	2.4	2
Density, grams per cubic centimeter	0.942	0.917
Comonomer content, percent	20	0
Vicat softening point, °F	138	194
Tensile strength, psi	1620	1850
Elongation, percent	720	650
Hardness, Shore D	35	46
Flexural stiffness psi	4000	18,500
Stress-cracking resistance (hostapal at 50°C)	no failure in two weeks	90 % failures in 1 day
Dielectric constant at 100 kilohertz	3.1	2.3
Dissipation factor at 100 kilohertz	0.015	0.0002
Low-temperature brittleness	no failures to -76°C	10 % failures to -76°C

a. Reprinted from "Plastics Technology", February, 1980.

EMA also has the valuable properties of low melt temperatures when used with conventional processing equipment, good melt adhesion to a wide variety of substrates, good heat sealability and unexpectedly high thermal stability when compared to other olefin based polymers. EMA pellets are not hydrophilic

as are some of the other copolymers and consequently it can be stored and handled in normal containers and resin silos without the fear of water absorption.

The main source of thermoplastic EMA polymers in the United States is Gulf Oil Chemicals Company, Orange, Texas, who produce the base resin at costs in the order of \$0.59/pound. Applications for this polymer include high strength films for food and packaging applications, disposable "rubber" gloves, and co-extruded films with other resins for heat seal applications. Gulf Oil Chemicals Company produce three commercial grades of EMA that vary in melt index and additives. The three grades compare as follows:

	<u>EMA Grade Number</u>		
	<u>2205</u>	<u>2255*</u>	<u>TD-938</u>
Melt Index (ASTM D-1238-E)	2.0	2.4	6.0
Optical Transmission Method ASTM 424-A	89.6%	89.8%	88.1%
Comonomer Content	20%	17%	20%
Refractive Index, n_D	1.49	1.49	1.49

*Contains anti-block agent, lubricant.

Other commercial sources of EMA resins were also surveyed due to the promising characteristics of this material. Two others were identified; Northern Petrochemical Company, Omaha, Nebraska and E. I. DuPont de Nemours, Wilmington, Delaware. Northern Petrochemical's resin is referred to as "Specialty Resin 1230" and has a melt index of 12 gms/10min. and a Shore A hardness value of 40. This resin will not be explored under the JPL program due to the fact that it is currently a "foreign source" material, being prepared by BASF Corporation, Baden, Germany and only distributed in the United States. The other EMA resin available from DuPont has the tradename "Vamac N-123" and is an opaque masterbatch ethylene/acrylic elastomer containing fumed silica, stabilizers and processings aids. It is not suitable for use as a pottant due to its negligible light transmission.

Experiments were conducted to determine if curable lamination compounds could be prepared from EMA resins. The Gulf product 2205 was used as a starting point and cure trials were run with high temperature aliphatic peroxides at a level of 1.5% by weight. The peroxide was blended into the resin on a heated (100°C) two roll mill for a period of five minutes. The formulation was then removed and plaques were compression molded at 150°C for 20 minutes. Gel was subsequently determined by extraction with hot toluene. The following results were obtained:

<u>Peroxide</u>	<u>Half-Life</u>	<u>Gel Content</u>
Lupersol 101	138°C	63.4 %
Lupersol 231	112°C	79.5 %
Lupersol 130	149°C	0 %
Vulcup-R ^a	137°C	72 %

-
- a. Vulcup-R is not an aliphatic peroxide and is included for comparison of cure efficiencies only.

Lupersol 231 was selected as the peroxide for use in complete formulations incorporating antioxidants and ultraviolet stabilizers. Due to the demonstrated efficiency of the formulation, the same stabilizer compounds used in the EVA formulation were used in the trial EMA formulations, as follows:

EMA, base resin	100 parts
Lupersol 231	1.5 parts
Cyasorb UV-531	0.3 parts
Tinuvin 770	0.1 parts
Naugard-P	0.2 parts

This formulation was tested with each of the three Gulf EMA polymers and resulted in consistently high gel values of 76-68%.

A fully compounded version of EMA (formulation A11877) was then run through the Brabender laboratory extruder to determine the processing conditions required to produce an extruded sheet suitable for the lamination approach to module fabrication. As with the EVA counterpart, the resin pellets (type 2205) were tumble blended with the peroxide and stabilizing

additives and run directly into the hopper of the extruder. The resulting sheet materials was of good quality, more easily controllable than EVA and could be extruded in thinner gauges. Extrusion proceeded smoothly at a barrel temperature of 100°C, a die temperature of approximately 80°C, and a back pressure of 1,200 psi. The throughput was steady and approximately the same speed as the EVA, with a barrel residence time of approximately 3-4 minutes.

Sheet resulting from this extrusion procedure was cured and analyzed for gel content. A low gel content of only 40% resulted. This is felt to be due to the higher melt viscosity of the EMA resin and insufficient blending of the peroxide during the extrusion process. This problem was expected to disappear with the use of the large (2 1/2") extruder and higher melt index resin.

The higher melt index resin (TD 938) was ordered from Gulf Oil Chemicals, Inc. in sufficient quantity to reevaluate the formulation on a laboratory scale and also for the large trial run. This new material (melt index 6 as opposed to 2) was compounded in the same manner as the previous copolymer and extruded without difficulty. Gel contents obtained with this formulation were found to be in the range of 74-78%. The blending properties of this polymer appear to be superior and subsequent formulations used it as the EMA base resin.

A brief experiment was also tried to determine if an alloy of EMA and EVA could be prepared that would have a melt index in a range more suitable for the compounding operation. A blend of EMA (TD-938) and EVA (Elvax-150) was prepared on a differential two roll rubber mill. The composition was adjusted for a melt index of 15 by using a composition of 74% EMA and 26% EVA. The two resins appear to be melt incompatible and result in an opaque polymer mass with poor transmission in molded sheets. This approach was discontinued.

The base resin was therefore changed to the material designated TD-938 with the higher melt flow value. This change was to facilitate more thorough compounding and possibly improve module fabrication due to the lower melt viscosity. The peroxide was also reevaluated in this formula and Lupersol-101 was found to be marginally more effective in raising the cured gel contents than the Lupersol 231. Its use is also advantageous because it has a higher thermal stability and will more easily tolerate shear/mixing in

the extrusion process without premature decomposition. The new formulation (Springborn number A13439) was cured for 30 minutes at 150°C and resulted in a gel content of 64%; 4% higher than the previous formulation using the first selection of peroxide.

This formulation was used for the preparation of the first pilot plant run to provide small quantities for industrial evaluation. The following chart summarizes the formulation, equipment and process parameters used in this extrusion operation:

EMA EXTRUSION RUN: SUMMARY

Formulation: No. A13439

Preparation: Blend 50 lb quantities in a 55 gallon drum by tumbling. Mix time minimum, 30 minutes. Product (hopper feed) is wet translucent pellets.

Formulation:	EMA Base resin TD-938	50 Lbs	100 Parts
	Lupersol 101	340 Gms	1.5 Parts
	Cyasorb UV-531	68.1 Gms	0.3 Parts
	Naugard-P	45.4 Gms	0.2 Parts
	Tinuvin 770	22.7 Gms	0.1 Parts

Extruder: Hartig, 2 1/2 inch barrel

Screw: Two stage compounding screw, 3.5:1 compression, 24:1 L/D

Screw Speed: Approximately 32 rpm

Die: Full width, 33"; set. gauge, 0.020"

Barrel and Die
Temperatures:

Zone:	1	2	3	4	5	8	9	10	11
Set:	195	195	195	195	195	185	185	185	185
Run:	200	205	220	220	200	210	200	200	195
(°C)	93°	96°	104°	104°	93°	99°	93°	93°	90°

Barrel

Adaptor

Die

Screen Pack: 20-100-80-20 mesh screens

Back Pressure: 3,000-3,200 psi

Blowers for Cooling: zones 2, 3, 4 on

Take up Rolls #2, 74°F, #3 and #4, 54°F

Take up Speed: approx. 4.2'/minute, appx. 250' linear/hour

Throughput: approx. 70-80 lbs/hour

The extrusion process proceeded smoothly without any special precautions, however attention was given to the extruder temperature profile to make sure that temperatures in excess of 110°C were not attained due to heat of shear

from the internal mixing operation. A two stage screw was used to facilitate the compounding of the additives into the polymer. The extruded sheet was uniform in gauge (18-20 mils), hazy and translucent in appearance and was wound onto a 3" diameter cardboard core for shipment and convenience in use.

No release paper interleaf was used to separate the plies of this product. The resin has very low surface tack and may be wound and unwound onto the cores with no difficulty.

Cure profiles were determined in the laboratory by curing compression molded plaques in a heated platten press for varying lengths of time and then measuring the gel content. The following table gives the results:

CURE PROFILE - EMA
Formulation Number A-13439

<u>Cure Time</u>	<u>Degree of Cure, % Gel</u>		
	<u>130°C</u>	<u>140°C</u>	<u>150°C</u>
10 minutes			0%
20 minutes			37%
30 minutes		Low Gel	53%
40 minutes	Low Gel	34%	63%
60 minutes	Low Gel	47%	65%

These results may be used as a general guide for the determination of the correct cure time required during module fabrication.

The degree of cure in the EMA based pottant is not as important as it is in the EVA pottant. The reason for curing pottant materials is to prevent destructive creep or flow that may occur in the module at elevated operating temperatures. EVA will creep very badly and flow off the module surface if it is not cured (vulcanized) and subsequently exposed to the upper limit use temperature (90°C). The requirement is not as stringent for the EMA based pottant, however. Two modules were prepared with both EMA 2205 and EMA TD-938 base resins without any cure additives at all. These modules were then placed in an air oven set for 90°C for a period of one

month. At the end of this period of time no creep of the pottant could be noticed and both modules were in the same condition as when they had been fabricated. Larger sized modules with uncured resin are currently undergoing the JPL thermal/humidity cycling test to verify the apparent lack of thermal creep. The necessity for curing the EMA and the required gel content (if any?) is also being determined by additional experiments at Springborn Laboratories.

Samples of the extruded EMA were compression molded into plaques and then cured between Teflon-FEP films to yield optically flat surfaces. Total integrated transmission values were then determined (ASTM E-424-A) over the range of 350 nm to 800 nm. The total transmission was found to be 90.5%.

Research quantities of EMA pottant are now available from Springborn Laboratories in extruded sheet form suitable for lamination experiments. Larger quantities will be available at a later date depending on the response from industry or will be prepared on a custom order basis.

Ethylene Vinyl Acetate (EVA)

The EVA pottant compound developed at Springborn Laboratories (designated A9918), is being used industrially in increasing quantities. Some difficulties are occasionally encountered in the cure process, however, due to variations in heat history when this material is used in different lamination schemes and equipment.

EVA cures through action of the thermal decomposition of the peroxide curing agent, whose decomposition rate increase logarithmically with increases in temperature. However, below 120 to 125°C, EVA itself is not capable of being cured even though there is slow thermal decomposition of the peroxide. Thus holding EVA at elevated temperatures below 120°C will not result in EVA cure, but will result in some depletion of the peroxide curing agent. The depletion quantity will be a function of holding time, and it can be presumed that there will exist some critical level of depletion such that the remaining quantity will be inadequate to cure the EVA when later heated to the peak curing temperature.

Due to the variation in processing requirements encountered in the industrial use of EVA, a series of tests were run to verify time/temperature cure conditions and examine the variations in cure efficiency. This

was done under laboratory conditions using a heated platten press as the heat source. Twenty mil thick plaques of EVA A9918 were pressed at different times and temperatures and then subsequently analyzed for gel content to indicate the degree of cure. The following table records the results:

CURE PROFILE - EVA
Formulation Number A9918

<u>Cure Time</u>	<u>Degree of Cure (% Gel)</u>		
	<u>130°C</u>	<u>140°C</u>	<u>150°C</u>
1 minute			2.1
2 minutes		1.0	4.1
5 minutes		11.8	21.1
10 minutes	1.0	23.5	63.2
15 minutes	2.3	59.3	88.3
30 minutes	3.4	68.2	
60 minutes	32.1	80.6	

As may be seen the 130°C temperature is ineffective in initiating cure. The 140°C temperature is effective, however it requires a one-hour period of time to reach an acceptable gel content. This is in accordance with the results obtained by some module manufacturers, based on recent contacts. The highest temperature, 150°C is the most suitable but still requires a full 15 minutes to develop a high degree of cure.

It is interesting to note that the times and temperatures resulting in acceptable polymer gel contents (over 70%) correlate well with the Half Life-Temperature Graph for the decomposition of Lupersol-101 in a benzene solution. The time/temperature requirements fall accurately (based on two points) on the curve of log peroxide half-life versus temperature. The curve is attached, Table I.

The time/temperature EVA cure relationship demonstrates that the curing time for EVA increases by approximately a factor of three for every 12°C decrease in cure temperature. Thus 20 minutes at 150°C requires 60 minutes at 138°C.

A method for the quantitative analysis of peroxide and the other compounding ingredients in A9918 is being developed using high pressure liquid chromatography (HPLC). This method will be used to determine the critical amount of peroxide required for cure at different points on the time/temperature curve; assess the amount of residual peroxide after cure; and be for quality control analysis of the compounded/extruded product.

IV. CONCLUSIONS

The butyl acrylate syrup system developed during this period of time appears to be well suited to the needs of the industrial fabricator. The long pot life and rapid cure time at low temperatures and insensitivity to moisture all lead to a very usable liquid casting system. Actual field performance will be assessed as soon as sufficient quantities of this pot-tant become available to ship to solar module manufacturers. Although suspected to be excellent, the outdoor weathering performance of this material is not known, however. Specimens of a prototype formulation have been exposed to almost 3,000 hours of RS/4 ultraviolet radiation with no decay in properties.

The formulation, as it stands now, is in the stage ready for industrial evaluation. The properties may be changed in the future to yield a "technically ready" pottant that represents the best possible combination of properties that the chemistry will permit and will be based on the recommendations of industrial users.

The EMA pottant film is similarly in the stage of readiness for industrial evaluation and the properties may also be modified at a later date in response to industrial requirements. The current EMA formulation does not appear to present any difficulties in terms of lamination and module processing. No broken cells have been noticed in any module prepared with this pottant. The current disadvantage with this pottant is that long cure times are required to develop high gel contents. Experiments in thermal creep have not demonstrated the necessity for any gel content at all, however. Possibly this resin may not have to be cured in order to be a useful encapsulation compound.

Samples are being provided for industrial evaluation at this time.

Appendix

TABLE I

Butyl Acrylate Potant: Initiator Studies
(Based on Standard Syrup Formulation Number A12805)

Initiator	Promoter	<u>Time to Cure (minutes)</u>			
		<u>20°C</u>	<u>35°C</u>	<u>45°C</u>	<u>55°C</u>
<u>0.5%</u>	<u>0.1%</u>				
Lupersol-225	None	NP	NP	NP	NP
Lupersol-225/ Benzoyl Peroxide	None	NP	NP	NP	NP
Lupersol-225/ Lupersol-11	None	NP	NP	32	21
<hr/>					
Benzoyl Peroxide	None	NP	NP	NP	47
Benzoyl Peroxide	Cobalt Naphthenate	NP	NP	NP	27
Benzoyl Peroxide	Stannous Octoate	NP	70	34	12
Benzoyl Peroxide	Zinc Octoate	NP	NP	NP	19
<hr/>					
Vazo - 33W	None	39	5.5	4	3
Vazo - 33W	Cobalt Naphthenate	58	-	-	-
Vazo - 33W	Stannous Octoate	30	4	3.5	2.5
Vazo - 33W	Dibutyl Tin Dilaurate	37	-	-	-
Vazo - 33W	Zinc Octoate	38	-	-	-
<hr/>					
Lupersol-11	None	NP	NP	21	12
Lupersol-11	Cobalt Naphthenate	NP	NP	5	2
Lupersol-11	Stannous Octoate	NP	29	11	5.5
Lupersol-11	Dibutyl Tin Dilaurate	NP	NP	18	7.5
Lupersol-11	Zinc Octoate	38	-	-	-

TABLE II

Butyl Acrylate - Final Formulations

Butyl Acrylate Syrup With 0.5% Alperox-F

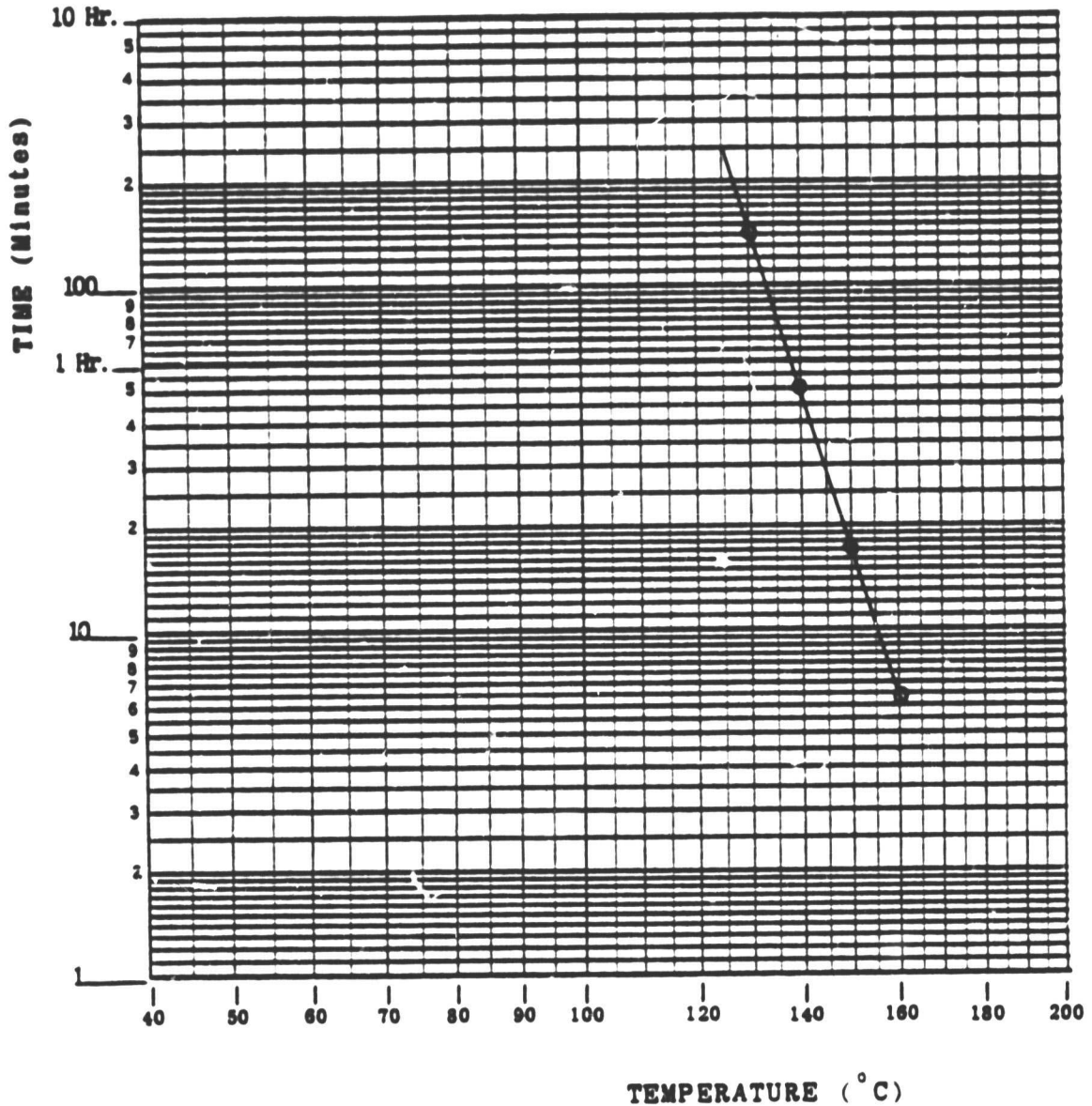
<u>Formulation Number</u>	<u>Additives</u>	<u>Room Temperature</u>	<u>50°C</u>	<u>60°C</u>	
A13446-					
1	Tinuvin-P, 0.5%	NP	-	20	
2	Tinuvin-P, 0.5% Promoter, 0.1%	NP	26	9	
3	5-Vinyl Tinuvin, 0.5%	NP	-	18	
4	5-Vinyl Tinuvin, 0.5% Promoter, 0.1%	NP	48	16	
5	Tinuvin-P 0.5% Tinuvin 770, 0.1%	NP	-	27	
6	Tinuvin-P, 0.5% Tinuvin 770, 0.1% Promoter, 0.1%	NP	26	11	
7	5-Vinyl Tinuvin, 0.5% Tinuvin 770, 0.1%	NP	-	25	
8	5-Vinyl Tinuvin, 0.5% Tinuvin 770, 0.1% Promoter, 0.1%	NP	60	14	
9	Tinuvin-P, 0.25% Tinuvin 770, 0.1%	NP	Over 60	24	
10	Tinuvin-P, 0.25% Tinuvin 770, 0.1% Promoter, 0.1%	NP	40	15	
11	Tinuvin-P, 0.25% Tinuvin 770, 0.05%	NP	Over 60	18	<u>70°C</u> 14
12	Tinuvin-P, 0.25% Tinuvin 770, 0.05% Promoter 0.1%	NP	42	15	11

NP = No polymerization noticed within an eight hour period of time.

TABLE III

EVA Cure Curve:

Peroxide Half - Life Temperature Graph^a



a. For Lupersol 101 peroxide; 2, 5-Dimethyl-2, 5-di(t-butyl peroxy)hexane

Source: "Evaluation of Organic Peroxides from Half-Life Data"
Bulletin 30-30; Lucidol Division, Pennwalt Corporation,
Buffalo, New York

Note: No cure of the EVA pottant occurs below 125°C.